NEET / IIT-JEE

Chemistry Question Bank

Part - 2

Compiler

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About The Compiler

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1. Electrochemistry

2. Chemical Equilibrium

3. Ionic Equilibrium

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5. Thermodynamics

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Note : The Examples And Questions In This Practice Bank Are Taken From Various Books, Institutions, Internet And Platforms

Electrochemistry

OT Ordinary Thinking

Objective Questions

Electrolytes and Electrolysis

1. Which of the following will not conduct electricity in aqueous solution **[AMU 1982, 83]**

(a) Copper sulphate (b) Sugar

(c) Common salt (d) None of these

2. Strong electrolytes are those which **[MNR 1983]**

(a) Dissolve readily in water

(b) Conduct electricity

(c) Dissociate into ions at high dilution

(d) Completely dissociate into ions at all dilutions

3. In aqueous solution, strong electrolytes **[AMU 1983, 84]**

(a) Are partially ionized

(b) Do not ionise

(c) Ionise almost completely

(d) Form polymers

4. An electrolyte **[KCET 1984; MP PET/PMT 1988]**

(a) Forms complex ions in solution

(b) Gives ions only when electricity is passed

(c) Possesses ions even in solid state

(d) Gives ions only when dissolved in water

5. Electrolytes when dissolved in water dissociates into ions because **[CPMT 1974, 78; MNR 1983]**

(a) They are unstable

(b) The water dissolves it

(c) The force of repulsion increases

(d) The forces of electrostatic attraction are broken down by water

6. Electrolyte can conduct electricity because

(a) Their molecules contain unpaired electrons, which are mobile

(b) Their molecules contain loosely held electrons which get free under the influence of voltage

(c) The molecules break up into ions when a voltage is applied

(d) The molecules are broken up into ions when the electrolyte is fused or is dissolved in the solvent

7. Which one of the following metals could not be obtained on electrolysis of aqueous solution of its salts **[IIT 1990]**

(a) Ag (b) Mg

(c) Cu (d) Cr

8. Which of the following aqueous solution will conduct an electric current quite well **[MP PMT 1987]**

(a) Glycerol (b) HCl

(c) Sugar (d) Pure water

9. On the electrolysis of aqueous solution of sodium sulphate, on cathode we get **[MP PMT 1992, 2002]**

(a) Na (b) H_2

(c) SO_2 (d) SO_3

10. Electrolysis involves oxidation and reduction respectively at **[CPMT 1973; AMU 1983; NCERT 1983, 84; MH CET 2001]**

(a) Anode and cathode (b) Cathode and anode

(c) At both the electrodes (d) None of the above

11. Which of the following compounds will not undergo decomposition on passing electricity through aqueous solution **[MP PET 2001]**

(a) Sugar (b) Sodium Chloride

(c) Sodium Bromide (d) Sodium Acetate

12. During the electrolysis of an electrolyte, the number of ions produced, is directly proportional to the **[AFMC 2002]**

(a) Time consumed

(b) Electro chemical equivalent of electrolysis

(c) Quantity of electricity passed

(d) Mass of electrons

13. When the sample of copper with zinc impurity is to be purified by electrolysis, the appropriate electrodes are **[AIEEE 2002]**

	Cathode	**Anode**
(a)	Pure zinc	Pure copper
(b)	Impure sample	Pure copper
(c)	Impure zinc	Impure sample
(d)	Pure copper	Impure sample

14. In the electrolytic cell, flow of electrons is from **[IIT Screening 2003]**

(a) Cathode to anode in solution

(b) Cathode to anode through external supply

(c) Cathode to anode through internal supply

(d) Anode to cathode through internal supply

15. An electric current is passed through an aqueous solution of the following. Which one shall decompose **[NCERT 1972]**

(a) Urea (b) Glucose

(c) $AgNO_3$ (d) Ethyl alcohol

16. The electric conduction of a salt solution in water depends on the

(a) Shape of its molecules

(b) Size of its molecules

(c) Size of solvent molecules

(d) Extent of its ionization

17. A solution of sodium sulphate in water is electrolysed using inert electrodes. The products at the cathode and anode are respectively **[IIT 1987,96]**

(a) H_2, O_2 (b) O_2, H_2

(c) O_2, Na (d) O_2, SO_2

18. On electrolysing a solution of dilute H_2SO_4 between platinum electrodes, the gas evolved at the anode is **[NCERT 1977, 79; MNR 1980; CBSE PMT 1992]**

(a) SO_2 (b) SO_3

(c) O_2 (d) H_2

19. The addition of a polar solvent to a solid electrolyte results in **[NCERT 1973]**

(a) Polarization (b) Association

(c) Ionization (d) Non-liberation of heat

20. During the electrolysis of fused $NaCl$, which reaction occurs at anode **[NCERT 1973; AFMC 1992; MP PMT 2002]**

(a) Chloride ions are oxidized

(b) Chloride ions are reduced

(c) Sodium ions are oxidised

(d) Sodium ions are reduced

21. The amount of ion discharged during electrolysis is not directly proportional to **[NCERT 1973]**

(a) Resistance

(b) Time

(c) Current

(d) Chemical equivalent of the ion

22. Electrolysis of aqueous HCl solution produces **[CPMT 1987]**

(a) H_2 gas at the anode

(b) H_2 gas at the cathode

(c) Cl_2 gas at the cathode

(d) Cl_2 and O_2 gases both at the anode

23. During electrolysis of $NaCl$ solution, part of the reaction is $Na^+ + e^- \rightarrow Na$. This is termed as **[NCERT 1984]**

(a) Oxidation (b) Reduction

(c) Deposition (d) Cathode reaction

24. When a solution of an electrolyte is heated the conductance of the solution **[KCET 1991]**

(a) Increases because of the electrolyte conducts better

(b) Decreases because of the increased heat

(c) Decreases because of the dissociation of the electrolyte is suppressed

(d) Increases because the electrolyte is dissociated more

25. The passage of current liberates H_2 at cathode and Cl_2 at anode. The solution is **[EAMCET 1979,87]**

(a) Copper chloride in water (b) $NaCl$ in water

(c) H_2SO_4 (d) Water

26. Pure water does not conduct electricity because it **[Manipal MEE 1995]**

(a) Has a low boiling point

(b) Is almost totally unionized

(c) Is neutral

(d) Is readily decomposed

27. Which is responsible for electrical conduction of molten sodium chloride **[MADT Bihar 1995]**

(a) Free electrons

(b) Free ions

(c) Free molecules

(d) Atoms of sodium and chlorine

28. In electrolysis of aqueous copper sulphate, the gas at anode and cathode is **[AFMC 1995]**

(a) O_2 and H_2 (b) SO_2 and H_2

(c) H_2 and O_2 (d) SO_3 and O_2

29. Use of electrolysis is **[AFMC 1995]**

(a) Electroplating (b) Electrorefining

(c) (a) and (b) both (d) None of these

30. Sodium is made by the electrolysis of a molten mixture of about 40% $NaCl$ and 60% $CaCl_2$ because **[CBSE PMT 1995]**

(a) $CaCl_2$ helps in conduction of electricity

(b) This mixture has a lower melting point than $NaCl$

(c) Ca^{++} can displace Na from $NaCl$

(d) Ca^{++} can reduce $NaCl$ to Na

31. Electrolysis is a process in which the cations and anions of the electrolyte are **[MP PET 1995]**

(a) Hydrated (b) Hydrolysed

(c) Charged (d) Discharged

32. Degree of ionisation of a solution depends upon **[BHU 1998]**

(a) Temperature (b) Nature of the electrolyte

(c) Nature of the solvent (d) None of these

33. Which of the following is non-electrolytes **[KCET (Med.) 1999]**

(a) $NaCl$ (b) $CaCl_2$

(c) $C_{12}H_{22}O_{11}$ (d) CH_3COOH

34. When a molten ionic hydride is electrolysed **[JIPMER 1999]**

(a) Hydrogen is liberated at the cathode

(b) Hydrogen is liberated at the anode

(c) There is no reaction

(d) H^- ions produced migrate to the cathode

35. During electrolysis, the species discharged at cathode are **[AFMC 2000]**

(a) Ions (b) Cation

(c) Anion (d) All of these

36. Electrolysis of molten anhydrous calcium chloride produces **[AIIMS 2000]**

(a) Calcium (b) Phosphorus

(c) Sulphur (d) Sodium

37. Which of the following properties of pure metal makes it more useful then the corresponding alloy **[RPET 2000]**

(a) It is harder than corresponding alloy

(b) It has high density

(c) It can be extracted easily

(d) It conducts heat and electricity easily

38. Which of the following liberate hydrogen on reaction with dilute H_2SO_4 **[Roorkee 2000]**

(a) Fe (b) Cu

(c) Al (d) Hg

39. Which one of the following material conducts electricity **[Kerala (Med.) 2003]**

(a) Diamond

(b) Crystalline sodium chloride

(c) Barium sulphate

(d) Fused potassium chloride

(e) Molten sulphur

40. Which of the following metals will give H_2 on reaction with $NaOH$ **[RPET 2003]**

(a) Mg (b) Ba

(c) Ca (d) Sr

41. Which of the following is not a non electrolyte **[J & K 2005]**

(a) Acetic acid (b) Glucose

(c) Ethanol (d) Urea

Faraday's law of electrolysis

1. Amount of electricity that can deposit 108 *gm* of silver from $AgNO_3$ solution is **[AFMC 1993; MP PMT 2004]**

(a) 1 ampere (b) 1 coulomb

(c) 1 faraday (d) None of the above

2. When 9.65 coulombs of electricity is passed through a solution of silver nitrate (atomic weight of $Ag = 107.87$ taking as 108) the amount of silver deposited is **[EAMCET 1992; KCET 2000]**

(a) 10.8 *mg* (b) 5.4 *mg*

(c) 16.2 *mg* (d) 21.2 *mg*

3. Three faradays electricity was passed through an aqueous solution of iron (II) bromide. The weight of iron metal (at. wt. = 56) deposited at the cathode (in *gm*) is **[EAMCET 1991]**

(a) 56 (b) 84

(c) 112 (d) 168

4. A silver cup is plated with silver by passing 965 coulombs of electricity, the amount of silver deposited is **[EAMCET 1990; MP PET 1994, 97]**

(a) 9.89 *g* (b) 107.87 *g*

(c) 1.0787 *g* (d) 1.002 *g*

5. The atomic weight of Al is 27. When a current of 5 Faradays is passed through a solution of Al^{+++} ions, the weight of Al deposited is **[NCERT 1984]**

(a) 27 *gm* (b) 36 *gm*

(c) 45 *gm* (d) 39 *gm*

6. An apparatus used for the measurement of quantity of electricity is known as a **[BHU 1979]**

(a) Calorimeter (b) Cathetometer

(c) Coulometer (d) Colorimeter

7. The unit of electrochemical equivalent is **[EAMCET 1980]**

(a) *Gram* (b) *Gram/ampere*

(c) *Gram/coulomb* (d) *Coulomb/gram*

8. A certain current liberated 0.504 *gm* of hydrogen in 2 hours. How many grams of copper can be liberated by the same current flowing for the same time in a copper sulphate solution **[NCERT 1973, 77; CPMT 1979, 89; AIIMS 1998]**

(a) 12.7 *gm* (b) 15.9 *gm*

(c) 31.8 *gm* (d) 63.5 *gm*

9. What weight of copper will be deposited by passing 2 Faradays of electricity through a cupric salt (Atomic weight of *Cu* = 63.5) **[NCERT 1975; CPMT 1977, 79]**

(a) 2.0 *gm* (b) 3.175 *gm*

(c) 63.5 *gm* (d) 127.0 *gm*

10. If the current is passed into the solution of an electrolyte **[AIIMS 1979]**

(a) Anions move towards anode, cations towards cathode

(b) Anions and cations both move towards anode

(c) Anions move towards cathode, cations towards anode

(d) No movement of ions takes place

11. Unit of Faraday is

(a) Ampere (b) Coulomb

(c) Coulomb $mole^{-1}$ (d) Coulomb Sec^{-1}

12. On passing 0.1 Faraday of electricity through aluminium chloride, the amount of aluminium metal deposited on cathode is $(Al = 27)$ **[MP PMT 1991]**

(a) 0.9 *gm* (b) 0.3 *gm*

(c) 0.27 *gm* (d) 2.7 *gm*

13. Which of the following represents the first law of Faraday **[MP PMT 1991]**

(a) $E = mc^2$ (b) $E = hv$

(c) $m = ect$ (d) $PV = nRT$

14. 5 amperes is passed through a solution of zinc sulphate for 40 minutes. Find the amount of zinc deposited at the cathode **[CBSE PMT 1996]**

(a) 40.65 *gm* (b) 4.065 *gm*

(c) 0.4065 *gm* (d) 65.04 *gm*

15. In an electroplating experiment $m\ g$ of silver is deposited, when 4 amperes of current flows for 2 minutes. The amount (in gms) of silver deposited by 6 amperes of current flowing for 40 seconds will be **[MNR 1991]**

(a) $4m$ (b) $m/2$

(c) $m/4$ (d) $2m$

16. On passing 3 *ampere* of electricity for 50 minutes, 1.8 *gram* metal deposits. The equivalent mass of metal is **[MP PMT 1992]**

(a) 20.5 (b) 25.8

(c) 19.3 (d) 30.7

17. The desired amount of charge for obtaining one mole of Al from Al^{3+}

(a) $3 \times 96500\ C$ (b) $96500\ C$

(c) $\frac{96500}{3} C$ (d) $\frac{96500}{2} C$

18. On passing one faraday of electricity through the electrolytic cells containing Ag^{+}, Ni^{+2} and Cr^{+3} ions solution, the deposited $Ag\,(At.\,wt. = 108)$, $Ni(At.wt. = 59)$ and $Cr\,(At.wt. = 52)$ is **[AIIMS 1982]**

	Ag	Ni	Cr
(a)	108 *gm*	29.5 *gm*	17.3 *gm*
(b)	108 *gm*	59.0 *gm*	52.0 *gm*
(c)	108.0 *gm*	108.0 *gm*	108.0 *gm*
(d)	108 *gm*	117.5 *gm*	166.0 *gm*

19. One Faraday of electricity when passed through a solution of copper sulphate deposits **[CPMT 1978]**

(a) 1 *mole* of Cu (b) 1 *gm* atom of Cu

(c) 1 *molecule* of Cu (d) 1 *gm* equivalent of Cu

20. When 1 coulomb of charge is passed through electrolyte solution, then the mass deposited is equal to

(a) Equivalent weight

(b) Atomic weight

(c) Electrochemical equivalent

(d) Chemical equivalent

21. The platinum electrodes were immersed in a solution of cupric sulphate and electric current passed through the solution. After some time it was found that colour of copper sulphate disappeared with evolution of gas at the electrode. The colourless solution contains **[NCERT 1984]**

(a) Platinum sulphate (b) Copper hydroxide

(c) Copper sulphate (d) Sulphuric acid

22. On passing C ampere of electricity through a electrolyte solution for t second, m *gram* metal deposits on cathode. The equivalent weight E of the metal is **[MP PMT 1990]**

(a) $E = \frac{C \times t}{m \times 96500}$ (b) $E = \frac{C \times m}{t \times 96500}$

(c) $E = \frac{96500 \times m}{C \times t}$ (d) $E = \frac{C \times t \times 96500}{m}$

23. How many Faradays are required to generate one gram atom of magnesium from $MgCl_2$ **[MADT Bihar 1982]**

(a) 1 (b) 2

(c) 3 (d) 4

24. To deposit 0.6354 *gm* of copper by electrolysis of aqueous cupric sulphate solution, the amount of electricity required (in coulombs) is **[MP PMT 1989]**

(a) 9650 (b) 4825

(c) 3860 (d) 1930

25. In electrolysis of a fused salt, the weight of the deposit on an electrode will not depend on **[CPMT 1973]**

(a) Temperature of the bath

(b) Current intensity

(c) Electrochemical equivalent of ions

(d) Time for electrolysis

26. Faraday's laws of electrolysis will fail when **[NCERT 1971]**

(a) Temperature is increased

(b) Inert electrodes are used

(c) A mixture of electrolytes is used

(d) In none of these cases

27. According to the first law of Faraday, the weight of a substance discharge at the electrode is

(a) $W = ZQ$ (b) $W = eF$

(c) $W = \frac{Z}{F} It$ (d) $W = ZI$

28. When 0.04 faraday of electricity is passed through a solution of $CaSO_4$, then the weight of Ca^{2+} metal deposited at the cathode is **[BHU 1996]**

(a) 0.2 *gm* (b) 0.4 *gm*

(c) 0.6 *gm* (d) 0.8 *gm*

29. A current 2.0 *A* is passed for 5 hours through a molten metal salt deposits 22 *g* of metal (At. wt. =177). The oxidation state of the metal in the metal salt is **[KCET 1996]**

(a) + 1 (b) + 2

(c) + 3 (d) + 4

30. How many atoms of calcium will be deposited from a solution of $CaCl_2$ by a current of 25 milliamperes flowing for 60 seconds **[BHU 1999]**

(a) 4.68×10^{18} (b) 4.68×10^{15}

(c) 4.68×10^{12} (d) 4.68×10^{9}

31. On passing 0.5 faraday of electricity through $NaCl$, the amount of Cl deposited on cathode is

[BHU 1997; RPET 1999]

(a) 35.5 *gm* (b) 17.75 *gm*

(c) 71 *gm* (d) 142 *gm*

32. What is the amount of chlorine evolved when 2 amperes of current is passed for 30 minutes in an aqueous solution of $NaCl$ **[BHU 1998; AIIMS 1999]**

(a) 66 *g* (b) 1.32 *g*

(c) 33 *g* (d) 99 *g*

33. On passing a current through KCl solution, $19.5\,g$ of potassium is deposited. If the same quantity of electricity is passed through a solution of aluminium chloride, the amount of aluminium deposited is **[EAMCET 1997]**

(a) 4.5 *g* (b) 9.0 *g*

(c) 13.5 *g* (d) 27 *g*

(e) None is correct

34. Electrolysis rules of Faraday's states that mass deposited on electrode is proportional to **[CBSE PMT 2000]**

(a) $m \propto I^2$ (b) $m \propto Q$

(c) $m \propto Q^2$ (d) None of these

35. A current being passed for two hour through a solution of an acid liberating 11.2 *litre* of oxygen at NTP at anode. What will be the amount of copper deposited at the cathode by the same current when passed through a solution of copper sulphate for the same time **[BVP 2003]**

(a) 16 *g* (b) 63 *g*

(c) 31.5 *g* (d) 8 *g*

36. In a metal oxide, there is 20% oxygen by weight. Its equivalent weight is **[Pb. PMT 2000]**

(a) 40 (b) 64

(c) 72 (d) 32

37. On the basis of the information available from the reaction

$\frac{4}{3}Al + O_2 \rightarrow \frac{2}{3}Al_2O_3, \Delta G = -827 kJ mol^{-1}$ of O_2, the minimum *emf* required to carry out an electrolysis of Al_2O_3 is (F = 96500$C\ mol^{-1}$) **[CBSE PMT 2003]**

(a) 8.56 *V* (b) 2.14 *V*

(c) 4.28 *V* (d) 6.42 *V*

38. Then during electrolysis of a solution of $AgNO_3$, 9650 *coulombs* of charge pass through the electroplating bath, the mass of silver deposited in the cathode will be

[AIEEE 2003]

(a) 1.08 *g* (b) 10.8 *g*

(c) 21.6 *g* (d) 108 *g*

39. Total charge on 1 mole of a monovalent metal ion is equal to

[DPMT 2001]

(a) 9.65×10^4 Coulomb (b) 6.28×10^{18} Coulomb

(c) 1.6×10^{-19} Coulomb (d) None of these

40. When an electric current is passed through acidulated water 112 *ml* of hydrogen gas at N.T.P. collect at the cathode in 965 *seconds*. The current passed, in amperes is

[MNR 1991; UPSEAT 2001]

(a) 1.0 (b) 0.5

(c) 0.1 (d) 2.0

41. How much chlorine will be liberated on passing one *ampere* current for 30 *minutes* through *NaCl* solution **[BVP 2003]**

(a) 0.66 *mole* (b) 0.33 *mole*

(c) 0.66 *gm* (d) 0.33 *gm*

42. The number of electrons involved in redox reactions when a Faraday of electricity is passed through an electrolyte in solution is **[NCERT 1982; Pb. PMT 2002]**

(a) 6×10^{23} (b) 6×10^{-23}

(c) 96500 (d) 8×10^{19}

43. Coulomb is equal to **[Orissa JEE 2002]**

(a) *ampere* × *second*
(b) *ampere* × *minute*
(c) *watt* × *second*
(d) *volt* × *second*

44. The energy required to release 1 electron from He^+ is.......

[Orissa JEE 2002]

(a) + 54.4 *eV*
(b) – 13.6 *eV*
(c) + 27.2 *eV*
(d) Cannot be predicted

45. Faraday's laws of electrolysis are related to the **[IIT 1983]**

(a) Atomic number of cation
(b) Atomic number of anion
(c) Equivalent weight of the electrolyte
(d) Speed of the cation

46. The electric charge for electrode decomposition of one gram equivalent of a substance is **[IIT 1984; KCET 1992]**

(a) One ampere per second
(b) 96500 coulombs per second
(c) One ampere for one hour
(d) Charge on one mole of electrons

47. The number of electrons passing per second through a cross-section of copper wire carrying 10^{-6} *amperes* of current per second is found to be **[EAMCET 1985]**

(a) 1.6×10^{-19}
(b) 6×10^{-35}
(c) 6×10^{-16}
(d) 6×10^{12}

48. The electrolytic cells, one containing acidified ferrous chloride and another acidified ferric chloride are connected in series. The ratio of iron deposited at cathodes in the two cells when electricity is passed through the cells will be

[CPMT 1989]

(a) 3 : 1
(b) 2 : 1
(c) 1 : 1
(d) 3 : 2

49. When 96500 coulomb of electricity is passed through a copper sulphate solution, the amount of copper deposited will be **[MP PMT 1996]**

(a) 0.25 *mol*
(b) 0.50 *mol*
(c) 1.00 *mol*
(d) 2.00 *mol*

50. During electrolysis of fused aluminium chloride $0.9\,gm$ of aluminium was deposited on the cathode. The volume of chlorine liberated at the anode will be

(a) 2.24 *litres*
(b) 11.2 *litres*
(c) 1.12 *litres*
(d) 5.6 *litres*

51. Faraday has the dimensions of **[MP PET 1995]**

(a) Coulombs
(b) Coulomb equivalent
(c) Coulomb per equivalent
(d) Coulomb per degree Kelvin

52. The required charge for one equivalent weight of silver deposite on cathode is

[Roorkee 1995]

(a) $9.65 \times 10^7\,C$
(b) $9.65 \times 10^4\,C$
(c) $9.65 \times 10^3\,C$
(d) $9.65 \times 10^5\,C$

53. 96500 *coulombs* of electric current liberates from $CuSO_4$ solution **[MP PMT 1995]**

(a) $63.5\,gm Cu$
(b) $31.75\,gm Cu$
(c) $96500\,gm Cu$
(d) $100\,gm Cu$

54. A current of strength 2.5 *amp* was passed through $CuSO_4$ solution for 6 minutes 26 seconds. The amount of copper deposited is

(Atomic weight of $Cu = 63.5$)

(1 faraday = 96500 coulombs)

[EAMCET 1989; MP PET 1994]

(a) 0.3175 *g*
(b) 3.175 *g*
(c) 0.635 *g*
(d) 6.35 *g*

55. A certain quantity of electricity is passed through an aqueous solution of $AgNO_3$ and cupric salt solution connected in series. The amount of Ag deposited is $1.08\,gm$, the amount of copper deposited is (atomic weight of *Cu* = 63.5; *Ag* = 108)

[EAMCET 1986]

(a) 0.6454 *g*
(b) 6.354 *g*
(c) 0.3177 *g*
(d) 3.177 *g*

56. The number of electrons required to deposit 1*gm* atom of aluminium (at. wt. = 27) from a solution of aluminium chloride will be (where *N* is Avogadro's number)

[AIIMS 1992]

(a) 1 *N*
(b) 2 *N*
(c) 3 *N*
(d) 4 *N*

57. Three faradays of electricity are passed through molten Al_2O_3, aqueous solution of $CuSO_4$ and molten $NaCl$ taken in different electrolytic cells. The amount of Al, Cu and Na deposited at the cathodes will be in the ratio of

[BHU 1990]

(a) 1 mole : 2 mole : 3 mole
(b) 3 mole : 2 mole : 1mole
(c) 1 mole : 1.5 mole : 3 mole
(d) 1.5 mole : 2 mole : 3 mole

58. An electrolytic cell contains a solution of Ag_2SO_4 and have platinum electrodes. A current is passed until 1.6 *gm* of O_2 has been liberated at anode. The amount of silver deposited at cathode would be

[CPMT 1971]

(a) 107.88 *gm*
(b) 1.6 *gm*
(c) 0.8 *gm*
(d) 21.60 *gm*

59. The aqueous solution of which of the following decomposes on passing electric current **[EAMCET 1973]**

(a) Canesugar (b) Urea

(c) Methanol (d) Potassium iodide

60. The number of Faradays needed to reduce 4 *gram* equivalents of Cu^{++} to Cu metal will be **[BHU 1981]**

(a) 1 (b) 2

(c) 1/2 (d) 4

61. When electricity is passed through the solution of $AlCl_3$, $13.5\ gm$ of Al are deposited. The number of Faraday must be

[NCERT 1974; MP PET 1992; MP PMT 1994]

(a) 0.50 (b) 1.00

(c) 1.50 (d) 2.00

62. The value of one Faraday is

[AMU 1983; AFMC 1989; MP PET 2001]

(a) $95500\ C\ mol^{-1}$ (b) $96550\ C\ mol^{-1}$

(c) $96500\ C\ mol^{-1}$ (d) $98500\ C\ mol^{-1}$

63. The quantity of electricity needed to liberate 0.5 gram equivalent of an element is **[CPMT 1988; MP PMT 1997]**

(a) 48250 *Faradays* (b) 48250 *Coulombs*

(c) 193000 *Faradays* (d) 193000 *Coulombs*

64. The number of coulombs required for the deposition of 107.870 *g* of silver is **[MP PET/PMT 1998]**

(a) 96,500 (b) 48,250

(c) 1,93,000 (d) 10,000

65. When one of ampere current flows for $1\ sec$ through a conductor, this quantity of electricity is known as

[MP PMT 1993]

(a) Faraday (b) Coulomb

(c) E.M.F. (d) Ohm

66. The mass deposited at an electrode is directly proportional to

[CPMT 1974; AFMC 1987; MP PET 2000]

(a) Atomic weight (b) Equivalent weight

(c) Molecular weight (d) Atomic number

67. From the solution of which of the following one faraday of electricity will liberate one gram atom of metal

[MHCET 1999; MP PET 1993,2000; AFMC 2000]

(a) $NaCl$ (b) $BaCl_2$

(c) $CuSO_4$ (d) $AlCl_3$

68. On electrolysis, 1 mole of aluminium will be deposited from its molten salt by **[MH CET 2000]**

(a) 3 moles of electrons (b) 4 moles of electrons

(c) 2 moles of electrons (d) 1 mole of electrons

69. The atomic weight of Fe is 56. The weight of *Fe* deposited from $FeCl_3$ solution by passing 0.6 Faraday of electricity is

[MH CET 2000]

(a) 5.6 *g* (b) 11.2 *g*

(c) 22.4 *g* (d) 33.6 *g*

70. 2.5 *F* of electricity are passed through a $CuSO_4$ solution. The number of *gm* equivalent of *Cu* deposited on anode is

[CPMT 1973; DPMT 1982; MP PMT 2001]

(a) Zero (b) 1.25

(c) 2.5 (d) 5.0

71. The equivalent weight of a certain trivalent element is 20. Molecular weight of its oxide is **[KCET 2003]**

(a) 152 (b) 56

(c) 168 (d) 68

72. Silver is removed electrically from 200 *ml* of a 0.1 *N* solution of $AgNO_3$ by a current of 0.1 *ampere*. How long will it take to remove half of the silver from the solution **[AMU 1999]**

(a) 16 *sec* (b) 96.5 *sec*

(c) 100 *sec* (d) 10 *sec*

73. In order to separate oxygen from one mole of H_2O the required quantity of coulomb would be **[RPET 1999]**

(a) 1.93×10^5 (b) 9.6×10^4

(c) 1.8 (d) 3.2

74. A current of 0.25*A* is passed through $CuSO_4$ solution placed in voltameter for 45 *minutes*. The amount of *Cu* deposited on cathode is (At weight of $Cu = 63.6$)

[BHU 2001]

(a) 0.20 *g* (b) 0.22 *g*

(c) 0.25 *g* (d) 0.30 *g*

75. Faraday constant **[KCET (Med.) 2001]**

(a) Is a numerical constant

(b) Depends on equivalent

(c) Depends upon the current passed

(d) Depends on the number of electrons

76. If 0.5 *amp* current is passed through acidified silver nitrate solution for 10 minutes. The mass of silver deposited on cathode, is (*eq*. *wt*. of silver nitrate = 108) **[AFMC 2001]**

(a) 0.235 *g* (b) 0.336 *g*

(c) 0.536 *g* (d) 0.636 *g*

77. The unit for the electric current is **[KCET (Med.) 2001]**

(a) *Ohm* (b) *Volt*

(c) *Ampere* (d) *Coulomb*

78. The quantity of electricity required to liberate $112\ cm^3$ of hydrogen at STP from acidified water is

[KCET (Med.) 2001]

(a) 0.1 *Faraday* (b) 1 *Faraday*
(c) 965 *Coulomb* (d) 96500 *Coulomb*

79. Which solution will show highest resistance during the passage of current **[BHU 2001]**
(a) 0.05 *N* $NaCl$ (b) 2 *N* $NaCl$
(c) 0.1 *N* $NaCl$ (d) 1 *N* $NaCl$

80. 4 *g* of copper was dissolved in concentrated nitric acid. The copper nitrate solution on strong heating gave 5 *g* of its oxide. The equivalent weight of copper is **[KCET 2004]**
(a) 23 (b) 32
(c) 12 (d) 20

81. The amount of silver deposited by passing 241.25 coulomb of current through silver nitrate solution is **[MHCET 2003]**
(a) 2.7 *g* (b) 2.7 *mg*
(c) 0.27 *g* (d) 0.54 *g*

82. When 1*F* of electricity is passed through acidulated water, O_2 evolved is **[MHCET 2004]**
(a) $11.2\ dm^3$ (b) $5.6\ dm^3$
(c) $22.4\ dm^3$ (d) $1.0\ dm^3$

83. Charge required to liberate 11.5 *g* sodium is **[AIIMS 1992; DCE 2002]**
(a) 0.5 *F* (b) 0.1 *F*
(c) 1.5 *F* (d) 96500 *coulombs*

84. In the electrolysis of water, one Faraday of electrical energy would evolve **[DCE 2004]**
(a) One mole of oxygen (b) One *g* atom of oxygen
(c) 8 *g* of oxygen (d) 22.4 *litres* of oxygen

85. In a galvanic cell, the electrons flow from **[KCET 2004]**
(a) Anode to cathode through the solution
(b) Cathode to anode through the solution
(c) Anode to cathode through the external circuit
(d) Cathode to anode through the external circuit

86. An electric current is passed through silver nitrate solution using silver electrodes. 10.79 *g* of silver was found to be deposited on the cathode if the same amount of electricity is passed through copper sulphate solution using copper electrodes, the weight of copper deposited on the cathode is **[Kerala PMT 2004]**
(a) 6.4 *g* (b) 2.3 *g*
(c) 12.8 *g* (d) 1.6 *g*
(e) 3.2 *g*

87. The law of electrolysis were proposed by **[CPMT 1982;Pb.CET 2003]**
(a) Kohlraush (b) Faraday
(c) Nernst (d) Berthelot

88. How many atoms of calcium will be deposited from a solution of $CaCl_2$ by a current 0.25 *mA* following for 60 seconds **[BHU 2004]**
(a) 4.68×10^{18} (b) 4.68×10^{15}
(c) 4.68×10^{12} (d) 4.68×10^{9}

89. The number of coulombs required to reduce 12.3 *g* of nitrobenzene to aniline **[UPSEAT 2003]**
(a) 115800 *C* (b) 5790 *C*
(c) 28950 *C* (d) 57900 *C*

90. During the process of electrolytic refining of copper, some metals present as impurity settle as 'anode mud'. These are **[AIEEE 2005]**
(a) *Sn* and *Ag* (b) *Pb* and *Zn*
(c) *Ag* and *Au* (d) *Fe* and *Ni*

91. A galvanic cell is set up from a zinc bar weighing 50*g* and 1.0*litre*, 1.0*M*, $CuSO_4$ solution. How long would the cell run, assuming it delivers a steady current of 1.0 *ampere* **[Roorkee 2000]**
(a) 48 *hrs* (b) 41 *hrs*
(c) 21 *hrs* (d) 1 *hr*

92. On passing electric current through molten aluminium chloride, 11.2 *litre* of Cl_2 is liberated at NTP at anode. The quantity of aluminium deposited at cathode is (at. *wt*. of *Al* = 27) **[JIPMER 2002]**
(a) 9 *g* (b) 18 *g*
(c) 27 *g* (d) 36 *g*

93. An electric current is passed through silver voltameter connected to a water voltameter. The cathode of the silver voltameter weighed 0.108 *g* more at the end of the electrolysis. The volume of oxygen evolved at STP is **[Kerala (Med.) 2003]**
(a) 56 cm^3 (b) 550 cm^3
(c) 5.6 cm^3 (d) 11.2 cm^3
(e) 22.4 cm^3

94. During electrolysis of aqueous $NaOH, 4\,g$ of O_2 gas is liberated at NTP at anode, H_2 gas liberated at cathode is **[CBSE PMT 1998]**
(a) 2.8 *litres* (b) 5.6 *litres*
(c) 11.2 *litres* (d) 22.4 *litres*

Conductor and conductance

1. Which one of the following statements is *correct*

[MP PET 1997]

(a) The oxidation number of oxygen in KO_2 is zero

(b) The specific conductance of an electrolyte solution decreases with increase in dilution

(c) Sn^{2+} oxidises Fe^{3+}

(d) $Zn/ZnSO_4$ is a reference electrode

2. In infinite dilutions, the equivalent conductances of Ba^{2+} and Cl^- are 127 and 76 $ohm^{-1} cm^{-1}\ eqvt^{-1}$. The equivalent conductivity of $BaCl_2$ at indefinite dilution is **[CBSE 2000]**

(a) 101.5 (b) 139.5

(c) 203.5 (d) 279.5

3. The factor which is not affecting the conductivity of any solution is

(a) Dilution (b) Nature of electrolyte

(c) Temperature (d) None of these

4. Specific conductance of 0.1 *m* nitric acid is $6.3 \times 10^{-2}\ ohm^{-1} cm^{-1}$. The molar conductance of solution is

[Kerala (Med.) 2003]

(a) 630 $ohm^{-1} cm^2 mole^{-1}$ (b) 315 $ohm^{-1} cm^2 mole^{-1}$

(c) 100 $ohm^{-1} cm^2 mole^{-1}$ (d) 6300 $ohm^{-1} cm^2 mole^{-1}$

(e) 63.0 $ohm^{-1} cm^2 mole^{-1}$

5. The conductivity of strong electrolyte is **[CPMT 2003]**

(a) Increase on dilution slightly

(b) Decrease on dilution

(c) Does not change with dilution

(d) Depend upon density of electrolytes itself

6. If *X* is the specific resistance of the solution and *M* is the molarity of the solution, the molar conductivity of the solution is given by **[Kurukshetra CEE 2002]**

(a) $\frac{1000X}{M}$ (b) $\frac{1000}{MX}$

(c) $\frac{1000M}{X}$ (d) $\frac{MX}{1000}$

7. Conductivity (unit Siemen's) is directly proportional to area of the vessel and the concentration of the solution in it and is inversely proportional to the length of the vessel then the unit of the constant of proportionality is **[AIEEE 2002]**

(a) $Sm\ mol^{-1}$ (b) $Sm^2\ mol^{-1}$

(c) $S^{-2} m^2\ mol$ (d) $S^2 m^2\ mol^{-2}$

8. If one end of a piece of a metal is heated, the other end becomes hot after some time. This is due to

[CBSE PMT 1995]

(a) Energised electrons moving to the other part of the metal

(b) Resistance of the metal

(c) Mobility of atoms in the metal

(d) Minor perturbation in the energy of atoms

9. Conductivity of a solution is directly proportional to

[KCET 1984]

(a) Dilution (b) Number of ions

(c) Current density (d) Volume of the solution

10. The increase in equivalent conductance of an electrolyte solution with dilution is due to the increase in

[MP PMT 1996]

(a) Ionic attraction

(b) Molecular attraction

(c) Degree of association of the electrolyte

(d) Degree of ionisation of the electrolyte

11. Which of the following conducts electricity **[AFMC 1995]**

(a) Fused $NaCl$ (b) CO_2

(c) Br_2 (d) Si

12. Which of the following shows electrical conduction

[CBSE PMT 1999; AIIMS 1999]

(a) Potassium (b) Graphite

(c) Diamond (d) Sodium

13. The unit of equivalent conductivity is

[CPMT 1999; BCECE 2005]

(a) *ohm cm*

(b) $ohm^{-1} cm^2 (gm\ equivalent)^{-1}$

(c) $ohm\ cm^2 (gm\ equivalent)$

(d) $S\ cm^{-2}$

14. It has been observed that gaseous hydrogen chloride is a very poor conductor of electricity but a solution of hydrogen chloride gas in water is a good conductor of electricity. This is due to the fact that **[NCERT 1976]**

(a) Water is good conductor of electricity

(b) Hydrogen chloride gas in water solution ionizes

(c) A gas is non-conductor but a liquid conducts electricity

(d) Gas does not obey Ohm's law whereas solution does

15. Electrolytic conduction differs from metallic conduction in that in the case of electrolytic conduction

[KCET 1987; Bihar CEE 1992]

(a) The resistance increases with increasing temperature

(b) The resistance decreases with increasing temperature

(c) The flow of current does not generate heat

(d) The resistance is independent of the length of the conductor

16. The electrolytic conductance is a direct measure of **[KCET 1990; CPMT 2003]**

(a) Resistance (b) Potential

(c) Concentration (d) Dissociation

17. Conductivity of a strong electrolyte **[KCET 1993]**

(a) Increases on dilution

(b) Does not change considerably on dilution

(c) Decreases on dilution

(d) Depends on density

18. Which of the following statements is not applicable to electrolytic conductors **[AIIMS 1991]**

(a) New products show up at the electrodes

(b) Ions are responsible for carrying the current

(c) Show a positive temperature coefficient for conductance

(d) A single stream of electrons flows from cathode to anode

19. Which one is not a conductor of electricity **[RPET 1999]**

(a) $NaCl$ (aqueous) (b) $NaCl$ (solid)

(c) $NaCl$ (molten) (d) Ag metal

20. Solid sodium chloride is bad conductor of electricity because

(a) It contains only molecules

(b) It does not possess ions

(c) The ions present in it are not free to move

(d) It does not contain free molecules

21. Which of the following is a poor conductor of electricity

[EAMCET 1992]

(a) CH_3COONa (b) C_2H_5OH

(c) $NaCl$ (d) KOH

22. The molar conductivity is maximum for the solution of concentration **[DCE 2002]**

(a) 0.001 *M* (b) 0.005 *M*

(c) 0.002 *M* (d) 0.004 *M*

23. The unit of molar conductivity is **[DCE 2002]**

(a) $\Omega^{-1}cm^{-2}mol^{-1}$ (b) $\Omega\ cm^{-2}mol^{-1}$

(c) $\Omega^{-1}cm^2mol^{-1}$ (d) $\Omega\ cm^2mol$

24. The highest electrical conductivity of the following aqueous solutions is of **[AIEEE 2005]**

(a) 0.1 *M* acetic acid (b) 0.1 *M* chloroacetic acid

(c) 0.1 *M* fluoroacetic acid (d) 0.1 *M* difluoroacetic acid

25. Given $l/a = 0.5cm^{-1}, R = 50ohm, N = 1.0$. The equivalent conductance of the electrolytic cell is **[Orissa JEE 2005]**

(a) $10\,ohm^{-1}cm^2gmeq^{-1}$ (b) $20\,ohm^{-1}cm^2gmeq^{-1}$

(c) $300\,ohm^{-1}cm^2gmeq^{-1}$ (d) $100ohm^{-1}cm^2\ gmeq^{-1}$

26. If equivalent conductance of $1M$ benzoic acid is $12.8ohm^{-1}cm^2$ and if the conductance of benzoate ion and H^+ ion are 42 and $288.42\,ohm^{-1}cm^2$ respectively. its degree of dissociation is **[DPMT 2005]**

(a) 39% (b) 3.9%

(c) 0.35% (d) 0.039%

27. The unit ohm^{-1} is used for **[J & K 2005]**

(a) Molar conductivity (b) Equivalent conductivity

(c) Specific conductivity (d) Conductivity

Cell constant and Electrochemical Cells

1. When electric current is passed through a cell having an electrolyte, the positive ions move towards the cathode and the negative ions towards the anode. If the cathode is pulled out of the solution **[AIIMS 1980]**

(a) The positive and negative ions will move towards the anode

(b) The positive ions will start moving towards the anode, the negative ions will stop moving

(c) The negative ions will continue to move towards the anode and the positive ions will stop moving

(d) The positive and negative ions will start moving randomly

2. If the half cell reaction $A + e^- \rightarrow A^-$ has a large negative reduction potential, it follows that **[MNR 1992; UPSEAT 2000, 02]**

(a) A is readily reduced (b) A is readily oxidised

(c) A^- is readily reduced (d) A^- is readily oxidised

3. Mark the *false* statement **[MP PET 1997]**

(a) A salt bridge is used to eliminate liquid junction potential

(b) The Gibbs free energy change, ΔG is related with electromotive force (E), as $\Delta G = -nFE$

(c) Nernst equation for single electrode potential is

$$E = E^o - \frac{RT}{nF}\ln a_{M^{n+}}$$

(d) The efficiency of a hydrogen oxygen fuel cell is 23%

4. The specific conductance of a 0.1 *N KCl* solution at $23^o C$ is $0.012ohm^{-1}\ cm^{-1}$. The resistance of cell containing the solution at the same temperature was found to be 55 *ohm*. The cell constant will be **[CBSE PMT 1999, 2000; KCET 2001]**

(a) $0.142 cm^{-1}$ (b) $0.66 cm^{-1}$

(c) $0.918 cm^{-1}$ (d) $1.12 cm^{-1}$

5. Which of the following reactions occurs at the cathode of a common dry cell **[NCERT 1978]**

(a) $Mn \rightarrow Mn^{2+} + 2e^-$

(b) $2MnO_2 + Zn^{2+} + 2e^- \rightarrow ZnMn_2O_4$

(c) $2ZnO_2 + Mn^{2+} + 2e^- \rightarrow MnZn_2O_4$

(d) $Zn \rightarrow Zn^{2+} + 2e^-$

6. In $Cu - Zn$ cell **[BHU 1981]**

(a) Reduction occurs at the copper cathode

(b) Oxidation occurs at the copper cathode

(c) Reduction occurs at the anode

(d) Chemical energy is converted to light energy

7. Which of the following reaction is used to make a fuel cell

[AIIMS 2003]

(a)
$Cd(s) + 2Ni(OH)_3(s) \rightarrow CdO(s) + 2Ni(OH) + H_2$

(b)
$Pb(s) + PbO_2(s) + 2H_2SO_4(aq) \rightarrow 2PbSO_4(s) +$

(c) $2H_2(g) + O_2(g) \rightarrow 2H_2O(l)$

(d)
$2Fe(s) + O_2(g) + 4H^+(aq) \rightarrow 2Fe^{2+}(aq) + 2H_2O$

8. When lead storage battery is charged **[MP PET 2003]**

(a) PbO_2 is dissolved

(b) H_2SO_4 is regenerated

(c) $PbSO_4$ is deposited on lead electrode

(d) Lead is deposited on lead electrode

9. When lead storage battery is charged

[MP PET 1993; MP PMT 2000]

(a) Lead dioxide dissolves

(b) Sulphuric acid is regenerated

(c) The lead electrode becomes coated with lead sulphate

(d) The amount of sulphuric acid decreases

10. The electrolytic decomposition of dilute sulphonic acid with platinum electrode in cathodic reaction is

[MNR 1988; UPSEAT 1999, 2002]

(a) Oxidation

(b) Reduction

(c) Oxidation and reduction both

(d) Neutralisation

11. Which colourless gas evolves, when NH_4Cl reacts with zinc in a dry cell battery **[Orissa JEE 2003]**

(a) NH_4 (b) N_2

(c) H_2 (d) Cl_2

12. Which of the substances Na, Hg, S, Pt and graphite can be used as electrodes in electrolytic cells having aqueous solutions **[AIIMS 1982]**

(a) Na, Pt and graphite (b) Na and Hg

(c) Pt and graphite only (d) Na and S only

13. In electrolysis of dilute H_2SO_4 using platinum electrodes

[DPMT 1983; IIT 1983; Kurukshetra CET 2002; AFMC 2005]

(a) H_2 is evolved at cathode

(b) NH_3 is produced at anode

(c) Cl_2 is obtained at cathode

(d) O_2 is produced

14. For cell reaction, $Zn + Cu^{2+} \rightarrow Zn^{2+} + Cu$, cell representation is **[BCECE 2005]**

(a) $Zn \mid Zn^{2+} \mid\mid Cu^{2+} \mid Cu$ (b) $Cu \mid Cu^{2+} \mid\mid Zn^{2+} \mid Zn$

(c) $Cu \mid Zn^{2+} \mid\mid Zn \mid Cu^{2+}$ (d) $Cu^{2+} \mid Zn \mid\mid Zn^{2+} \mid Cu$

15. Which one is not called a anode reaction from the following

(a) $Cl^- \rightarrow \frac{1}{2}Cl_2 + e^-$ (b) $Cu \rightarrow Cu^{++} + 2e^-$

(c) $Hg^+ \rightarrow Hg^{++} + e^-$ (d) $Zn^{2+} + 2e^- \rightarrow Zn$

16. A cell from the following which converts electrical energy into chemical energy

(a) Dry cell (b) Electrochemical cell

(c) Electrolytic cell (d) None of these

17. In the cell $Zn \mid Zn^{2+} \mid\mid Cu^{2+} \mid Cu$, the negative electrode is

[MP PMT 1995]

(a) Cu (b) Cu^{2+}

(c) Zn (d) Zn^{2+}

18. Which of the following statements is correct ? Galvanic cell converts **[KCET 1991; MP PMT 1993]**

(a) Chemical energy into electrical energy

(b) Electrical energy into chemical energy

(c) Metal from its elemental state to the combined state

(d) Electrolyte into individual ions

19. Hydrogen–oxygen fuel cells are used in space–craft to supply **[MP PMT 1993; MP PET 1999]**

(a) Power for heat and light

(b) Power for pressure

(c) Oxygen

(d) Water

20. The standard cell potential of $Zn \mid Zn^{2+}{}_{(aq)} \mid\mid Cu^{2+}{}_{(aq)} \mid Cu$ cell is 1.10 *V*. The maximum work obtained by this cell will be **[MP PET 2002]**

(a) 106.15 *kJ* (b) – 212.30 *kJ*

(c) – 318.45 *kJ* (d) – 424.60 *kJ*

21. The relationship between standard reduction potential of cell and equilibrium constant is shown by **[MP PET 2002]**

(a) $E^0_{cell} = \frac{n}{0.059} \log K_c$ (b) $E^0_{cell} = \frac{0.059}{n} \log K_c$

(c) $E^0_{cell} = 0.059 n \log K_c$ (d) $E^0_{cell} = \frac{\log K_c}{n}$

22. Consider the Galvanic cell $Zn^{\ominus} \mid ZnSO_4 \mid\mid CuSO_4 \mid Cu^{\oplus}$ the reaction at cathode is **[AMU 2000]**

(a) $Zn^{2+} + 2e^- \rightarrow Zn$

(b) $Cu^{2+} + 2e^- \rightarrow Cu$

(c) $Cu^{2+} + Zn \rightarrow Cu + Zn^{2+}$

(d) $Zn^{2+} + Cu \rightarrow Zn + Cu^{2+}$

23. The cell reaction $Cu + 2Ag^+ \rightarrow Cu^{+2} + Ag$ is best represented by **[AMU 2000]**

(a) $Cu_{(s)} \mid Cu^{+2}{}_{(aq)} \mid\mid Ag^+{}_{(aq)} \mid Ag_{(s)}$

(b) $Pt \mid Cu^{+2} \mid\mid Ag^+{}_{(aq)} \mid Ag_{(s)}$

(c) $Cu^{+2} \mid Cu \mid\mid Pt \mid Ag$

(d) None of the above representations

24. $\underset{\text{(anode)}}{Zn_{(s)} \mid Zn^{2+}{}_{(aq)}} \mid\mid \underset{\text{(cathode)}}{Cu^{2+}{}_{(aq)} \mid Cu_{(s)}}$ is **[Kerala (Engg.) 2002]**

(a) Weston cell (b) Daniel cell

(c) Calomel cell (d) Faraday cell

(e) Standard cell

25. The specific conductance of a solution is 0.2 $ohm^{-1} cm^{-1}$ and conductivity is 0.04 ohm^{-1}. The cell constant would be **[RPET 1999]**

(a) 1 cm^{-1} (b) 0 cm^{-1}

(c) 5 cm^{-1} (d) 0.2 cm^{-1}

26. If the conductance and specific conductance of a solution is one then its cell constant would be **[RPET 1999]**

(a) 1 (b) Zero

(c) 0.5 (d) 4

27. Saturated solution of KNO_3 is used to make 'salt-bridge' because **[IIT Screening 2002]**

(a) Velocity of K^+ is greater than that of NO_3^-

(b) Velocity of NO_3^- is greater than that of K^+

(c) Velocities of both K^+ and NO_3^- are nearly the same

(d) KNO_3 is highly soluble in water

28. In balancing the half reaction $S_2O_3^{2-} \rightarrow S_{(s)}$ the number of electrons that must be added is **[DPMT 2000]**

(a) 4 on the left (b) 3 on the right

(c) 2 on the left (d) 2 on the right

29. Which one of the following statement is true for a electrochemical cell **[Pb. PMT 1999; KCET 1999]**

(a) H_2 is cathode and Cu is anode

(b) H_2 is anode and Cu is cathode

(c) Reduction occurs at H_2 electrode

(d) Oxidation occurs at Cu electrode

30. In the reaction

$Cu(s) + 2Ag^+(aq) \rightarrow Cu^{2+}(aq) + 2Ag(s)$

The reduction half-cell reaction is **[AIIMS 1997]**

(a) $Cu + 2e^- \rightarrow Cu^{2-}$ (b) $Cu - 2e^- \rightarrow Cu^{2+}$

(c) $Ag^+ + e^- \rightarrow Ag$ (d) $Ag - e^- \rightarrow Ag^+$

31. Which of the following statements about galvanic cell is incorrect **[JIPMER 1997]**

(a) Anode is positive

(b) Oxidation occurs at the electrode with lower reduction potential

(c) Cathode is positive

(d) Reduction occurs at cathode

32. The molar conductances of $NaCl, HCl$ and CH_3COONa at infinite dilution are 126.45, 426.16 and $91\, ohm^{-1}\, cm^2\, mol^{-1}$ respectively. The molar conductance of CH_3COOH at infinite dilution is **[CBSE PMT 1997]**

(a) $201.28\, ohm^{-1}\, cm^2\, mol^{-1}$

(b) $390.71\, ohm^{-1} cm^2\, mol^{-1}$

(c) $698.28\, ohm^{-1}\, cm^2\, mol^{-1}$

(d) $540.48\, ohm^{-1} cm^2\, mol^{-1}$

33. The electrodes of a conductivity cell are $3 cm$ apart and have a cross-sectional area of $4 cm^2$. The cell constant of the cell (in cm^{-1}) is

(a) 4×3 (b) $4/3$

(c) $3/4$ (d) $9/4$

34. The anode half-reaction occurring during the discharge of a lead storage battery is

(a) $Pb(s) + SO_2 + O_2 \rightarrow PbSO_4(s)$

(b) $Pb(s) + SO_4^{2-}(aq) \rightleftharpoons PbSO_4(s) + 2e^-$

(c) $PbO_2(s) + 4H^+(aq) + 2e^- + SO_4^{2-}(aq) \rightleftharpoons PbSO_4(s) + 2H_2O$

(d) $Pb^{2+}(aq) + SO_4^{2-}(aq) \rightarrow PbSO_4(s)$

35. The unit of cell constant is **[MP PET 1996]**

(a) $ohm^{-1}\,cm^{-1}$ (b) $ohm\,cm$

(c) cm (d) cm^{-1}

36. In dry cell the reaction which takes place at the zinc anode is

[MP PET 1996]

(a) $Zn^{2+} + 2e^- \rightarrow Zn(s)$

(b) $Zn(s) \rightarrow Zn^{2+} + 2e^-$

(c) $Mn^{2+} + 2e^- \rightarrow Mn(s)$

(d) $Mn(s) \rightarrow Mn^+ + e^- + 1.5V$

37. The chemical reaction taking place at the anode of a cell is

[MP PET 1996]

(a) Ionisation (b) Reduction

(c) Oxidation (d) Hydrolysis

38. Which of the following reactions occurs at the cathode during the charging of a lead storage battery

[Manipal MEE 1995; MP PET 2002]

(a) $Pb^{2+} + 2e^- \rightarrow Pb$

(b) $Pb^{2+} + SO_4^{2-} \rightarrow PbSO_4$

(c) $Pb \rightarrow Pb^{2+} + 2e^-$

(d) $PbSO_4 + 2H_2O \rightarrow 2PbO_2 + 4SO_4^{2-} + 2e^-$

39. A depolarizer used in dry cell batteries is **[NCERT 1981]**

(a) Ammonium chloride (b) Manganese dioxide

(c) Potassium hydroxide (d) Sodium phosphate

40. When a lead storage battery is discharged

[IIT 1987; MP PMT 2004]

(a) SO_2 is evolved

(b) Lead sulphate is consumed

(c) Lead is formed

(d) Sulphuric acid is consumed

41. In electroplating, the article to be electroplated serves as

[AMU 1982, 83]

(a) Cathode (b) Electrolyte

(c) Anode (d) Conductor

42. The position of some metals in the electrochemical series in decreasing electropositive character is given as $Mg > Al > Zn > Cu > Ag$. What will happen, if a copper spoon is used to stir a solution of aluminium nitrate

[NCERT 1977]

(a) The spoon will get coated with Al

(b) An alloy of Cu and Al is formed

(c) The solution becomes blue

(d) There is no reaction

43. In a electrochemical cell **[AFMC 1989]**

(a) Potential energy changes into kinetic energy

(b) Kinetic energy changes into potential energy

(c) Chemical energy changes into electrical energy

(d) Electrical energy changes into chemical energy

44. In galvanic cell, the salt bridge is used to **[MP PMT 2002]**

(a) Complete the circuit

(b) Reduce the electric resistance in the cell

(c) Separate cathode from anode

(d) Carry salts for the chemical reaction

45. If a strip of Cu metal is placed in a solution of ferrous sulphate **[NCERT 1974; CPMT 1977; MP PET 2000]**

(a) Copper will precipitate out

(b) Iron will precipitate out

(c) Copper will dissolve

(d) No reaction will take place

46. Which of the following is not used to construct salt bridge

[MP PET 2003]

(a) CH_3COOK (b) KCl

(c) NH_4NO_3 (d) KNO_3

47. The reference electrode is made by using **[MP PMT 2002]**

(a) $ZnCl_2$ (b) $CuSO_4$

(c) $HgCl_2$ (d) Hg_2Cl_2

48. In a hydrogen – oxygen fuel cell, combustion of hydrogen occurs to **[AIEEE 2004]**

(a) Produce high purity water

(b) Create potential difference between the two electrodes

(c) Generate heat

(d) Remove adsorbed oxygen from electrode surfaces

49. $\lambda_{ClCH_2COONa} = 224\,ohm^{-1}cm^2gmeq^{-1}$,

$\lambda_{NaCl} = 38.2\,ohm^{-1}cm^2gmeq^{-1}$,

$\lambda_{HCl} = 203\,ohm^{-1}cm^2gmeq^{-1}$, What is the value of λ_{ClCH_2COOH}

[JEE Orissa 2004]

(a) $288.5\ ohm^{-1}cm^2gmeq^{-1}$

(b) $289.5\ ohm^{-1}cm^2gmeq^{-1}$

(c) $388.5\ ohm^{-1}cm^2gmeq^{-1}$

(d) $59.5\ ohm^{-1}cm^2gmeq^{-1}$

50. Which of the following statement is true for the electrochemical Daniel cell **[AIIMS 2004]**

(a) Electrons flow from copper electrode to zinc electrode

(b) Current flows from zinc electrode to copper electrode

(c) Cations move toward copper electrode which is cathode

(d) Cations move toward zinc electrode

51. Which of the following statement is true for an electrochemical cell **[Pb.CET 2002]**

(a) H_2 is cathode and Cu is anode

(b) H_2 is anode and Cu is cathode

(c) Reduction occurs at H_2 electrode

(d) Oxidation occurs at Cu electrode

52. Which of the following statements are true for an fuel cells

[DPMT 2004]

(a) They run till the reactants are active

(b) They are free from pollution

(c) They are more efficient

(d) All of the above

53. For gold plating, the electrolyte used is **[Pb.CET 2004]**

(a) $AuCl_3$ (b) $HAuCl_4$

(c) $k[Au(CN)_2]$ (d) None of these

54. The acid used in lead storage battery is **[Pb.CET 2003]**

(a) H_2SO_4 (b) H_3PO_4

(c) HCl (d) HNO_3

55. At 25°C specific conductivity of a normal solution of KCl is 0.002765 *mho*. The resistance of cell is 400 *ohms*. The cell constant is **[Pb.PMT 2004]**

(a) 0.815 (b) 1.016

(c) 1.106 (d) 2.016

56. Which of the following is used widely in the manufacture of lead storage battery **[BHU 2004]**

(a) Arsenic (b) Lithium

(c) Bismuth (d) Antimony

57. The chemical reaction, $2AgCl(s) + H_2(g) \rightarrow 2HCl(aq) + 2Ag(s)$ taking place in a galvanic cell is represented by the notation

[AIIMS 2005]

(a) $Pt \mid H_2(g), 1bar \mid 1M\ KCl(aq) \mid AgCl(s) \mid Ag(s)$

(b) $Pt(s) \mid H_2(g),\ 1bar \mid 1M\ HCl(aq) \mid \mid 1M\ Ag^+(aq) \mid Ag(s)$

(c) $Pt(s) \mid H_2(g),\ 1bar \mid 1M\ HCl(aq) \mid AgCl(s) \mid Ag(s)$

(d) $Pt(s) \mid H_2(g),\ 1bar \mid 1M\ HCl(aq) \mid Ag(s) \mid AgCl(s)$

58. If the Zn^{2+}/Zn electrode is diluted to 100 times then the change in e.m.f. **[DPMT 2005]**

(a) Increase of $59 mV$

(b) Decrease of $59 mV$

(c) Increase of $29.5 mV$

(d) Decrease of $29.5 mV$

59. If hydrogen electrode dipped in 2 solution of $pH = 3$ and $pH = 6$ and salt bridge is connected the e.m.f. of resulting cell is **[DPMT 2005]**

(a) 0.177 V (b) 0.3 V

(c) 0.052 V (d) 0.104 V

60. The tendency of an electrode to lose electrons is known as

[J & K 2005]

(a) Electrode potential (b) Reduction potential

(c) Oxidation potential (d) e.m.f.

61. When electric current is supplied through an ionic hydride of fused state, then **[Kerala CET 2005]**

(a) Hydrogen is obtained at anode

(b) Hydrogen is obtained at cathode

(c) No change

(d) Hydride ion moves towards cathode

(e) hydride ion present in solution

Electrode potential, E_{Cell}, Nernt equation and ECS

1. The hydrogen electrode is dipped in a solution of $pH = 3$ at 25^oC. The potential of the cell would be (the value of $2.303RT/F$ is 0.059 V) **[KCET 1993,2005]**

(a) 0.177 V (b) – 0.177 V

(c) 0.087 V (d) 0.059 V

2. The standard electrode potentials of Zn^{2+} / Zn and Ag^{+} / Ag are $-0.763 V$ and $+0.799 V$ respectively. The standard potential of the cell is **[KCET 1993]**

(a) 1.56 *V* (b) 0.036 *V*

(c) – 1.562 *V* (d) 0.799 *V*

3. The standard reduction potentials at $298 K$ for the following half reactions are given against each

$Zn^{2+}(aq.) + 2e \rightleftharpoons Zn(s)$; – 0.762

$Cr^{3+}(aq) + 3e \rightleftharpoons Cr(s)$; – 0.740

$2H^{+}(aq) + 2e \rightleftharpoons H_2(g)$; 0.00

$Fe^{3+}(aq) + e \rightleftharpoons Fe^{2+}(aq)$; 0.770

Which is the strongest reducing agent

[IIT 1981; MP PET/PMT 1988; MP PMT 1989; MH CET 2001]

(a) $Zn(s)$ (b) $Cr(s)$

(c) $H_2(g)$ (d) $Fe^{2+}(aq)$

4. When Zn piece is kept in $CuSO_4$ solution, the copper get precipitated due to standard potential of zinc is **[CPMT 1999]**

(a) > copper (b) < copper

(c) > sulphate (d) < sulphate

5. Which of the following metal does not react with the solution of copper sulphate **[CPMT 1999]**

(a) Mg (b) Fe

(c) Zn (d) Ag

6. A solution containing one mole per litre of each $Cu(NO_3)_2$, $AgNO_3$, $Hg_2(NO_3)_2$ and $Mg(NO_3)_2$, is being electrolysed by using inert electrodes. The values of standard electrode potentials in volts (reduction potentials) are $Ag / Ag^{+} = +0.80, 2Hg / Hg_2^{2+} = +0.79, Cu / Cu^{2+}$ $Mg / Mg^{2+} = -2.37$ with increasing voltage, the sequence of deposition of metals on the cathode will be

[IIT 1984; AMU 1999; Kerala PMT 2004]

(a) Ag, Hg, Cu, Mg (b) Mg, Cu, Hg, Ag

(c) Ag, Hg, Cu (d) Cu, Hg, Ag

7. The standard reduction electrode potentials of four elements are

$A = -0.250 V$ $B = -0.136 V$

$C = -0.126 V$ $D = -0.402 V$

The element that displaces A from its compounds is

(a) B (b) C

(c) D (d) None of these

8. The standard oxidation potential of zinc and silver in water at $298 K$ are

$Zn (s) \rightarrow Zn^{2+} + 2e^{-}; E = 0.76 V$

$Ag (s) \rightarrow Ag^{2+} + 2e^{-}; E = -0.80 V$

Which of the following reactions actually take place

[NCERT 1983, 84; KCET 2003]

(a) $Zn(s) + 2Ag^{+}(aq) \rightarrow Zn^{++}(aq) + 2Ag(s)$

(b) $Zn^{++}(aq) + 2Ag(s) \rightarrow 2Ag^{+}(aq) + Zn(s)$

(c) $Zn(s) + Ag(s) \rightarrow Zn^{++}(aq) + Ag^{+}(aq)$

(d) $Zn^{++}(aq) + Ag^{+}(aq) \rightarrow Zn(s) + Ag(s)$

9. Beryllium is placed above magnesium in the second group. Beryllium dust, therefore when added to $MgCl_2$ solution will

[CPMT 1977]

(a) Have no effect

(b) Precipitate Mg metal

(c) Precipitate MgO

(d) Lead to dissolution of Be metal

10. The name of equation showing relation between electrode potential (E) standard electrode potential (E^{o}) and concentration of ions in solution is

(a) Kohlrausch's equation (b) Nernst's equation

(c) Ohm's equation (d) Faraday's equation

11. The correct representation of Nernst's equation is

(a) $E_{M^{n+}/M} = E^{o}_{M^{n+}/M} + \dfrac{0.0591}{n} \log(M^{n+})$

(b) $E_{M^{n+}/M} = E^{o}_{M^{n+}/M} - \dfrac{0.0591}{n} \log(M^{n+})$

(c) $E_{M^{n+}/M} = E^{o}_{M^{n+}/M} + \dfrac{n}{0.0591} \log(M^{n+})$

(d) None of the above

12. Standard electrode potential of NHE at 298 K is

(a) 0.05 *V* (b) 0.1 *V*

(c) 0.00 *V* (d) 0.11 *V*

13. When a copper wire is placed in a solution of $AgNO_3$, the solution acquires blue colour. This is due to the formation of

[Roorkee 1989]

(a) Cu^{2+} ions

(b) Cu^{+} ions

(c) Soluble complex of copper with $AgNO_3$

(d) Cu^{-} ion by the reduction of Cu

14. Consider the reaction $M^{n+}_{(aq)} + ne^- \rightarrow M_{(s)}$. The standard reduction potential values of the elements M_1, M_2 and M_3 are $-0.34 V, -3.05 V$ and $-1.66 V$ respectively. The order of their reducing power will be **[NCERT 1990]**

(a) $M_1 > M_2 > M_3$
(b) $M_3 > M_2 > M_1$
(c) $M_1 > M_3 > M_2$
(d) $M_2 > M_3 > M_1$

15. $E^0 = \frac{RT}{nF}$ In K_{eq}. This is called

[CPMT 1988; MP PET 2000]

(a) Gibb's equation
(b) Gibb's–Helmholtz equation
(c) Nernst's equation
(d) Vander Waal's equation

16. Four alkali metals A, B, C and D are having respectively standard electrode potential as –3.05,–1.66,–0.40 and 0.80. Which one will be the most reactive

[MP PMT/PET 1988 ; CPMT 1983; MNR 1993; UPSEAT 2002]

(a) A
(b) B
(c) C
(d) D

17. Which one of the following metals cannot evolve H_2 from acids or H_2O or from its compounds

[MP PET/PMT 1988; CPMT 1996; AFMC 1998, 99; Pb. PET 1999; BVP 2003]

(a) Hg
(b) Al
(c) Pb
(d) Fe

18. Which one of the following reaction is not possible

[MP PMT 1991]

(a) $Fe + H_2SO_4 \rightarrow FeSO_4 + H_2$
(b) $Cu + 2AgNO_3 \rightarrow Cu(NO_3)_2 + 2Ag$
(c) $2KBr + I_2 \rightarrow 2KI + Br_2$
(d) $CuO + H_2 \rightarrow Cu + H_2O$

19. When a rod of metal A is dipped in an aqueous solution of metal B (concentration of B^{2+} ion being 1*M*) at $25^\circ C$, the standard electrode potentials are A^{2+}/A =–0.76 volts, B^{2+}/B = + 0.34 volts **[KCET 1992]**

(a) A will gradually dissolve
(b) B will deposit on A
(c) No reaction will occur
(d) Water will decompose into H_2 and O_2

20. The reaction $Zn^{2+} + 2e^- \rightarrow Zn$ has a standard potential of $-0.76 V$. This means **[KCET 1992]**

(a) Zn can't replace hydrogen from acids
(b) Zn is a reducing agent
(c) Zn is a oxidising agent
(d) Zn^{2+} is a reducing agent

21. $2H^+(aq) + 2e^- \rightarrow H_2(g)$. The standard electrode potential for the above reaction is (in volts) **[CPMT 1988]**

(a) 0
(b) + 1
(c) – 1
(d) None of these

22. K, Ca and Li metals may be arranged in the decreasing order of their standard electrode potentials as **[CPMT 1990]**

(a) K, Ca, Li
(b) Ca, K, Li
(c) Li, Ca, K
(d) Ca, Li, K

23. The correct order of chemical reactivity with water according to electrochemical series **[MP PMT 1991]**

(a) $K > Mg > Zn > Cu$
(b) $Mg > Zn > Cu > K$
(c) $K > Zn > Mg > Cu$
(d) $Cu > Zn > Mg > K$

24. EMF of cell

$Ni \mid Ni^{2+}(1.0 M) \mid\mid Au^{3+}(1.0 M) \mid Au$

(Where E^o for $Ni^{2+} \mid Ni$ is $-0.25 V$; E^o for $Au^{+3} \mid Au$ is $1.50 V$) is **[MP PET 1993; MP PMT 2000]**

(a) + 1.25 *V*
(b) $-1.75 V$
(c) + 1.75 *V*
(d) + 4.0 *V*

25. Oxidation and reduction take place in a cell, then its electromotive force will be **[RPET 1999]**

(a) Positive
(b) Negative
(c) Zero
(d) Stable

26. For a spontaneous reaction the ΔG, equilibrium constant (*K*) and E^o_{Cell} will be respectively **[AIEEE 2005]**

(a) $-ve, > 1, +ve$
(b) $+ve, > 1, -ve$
(c) $-ve, < 1, -ve$
(d) $-ve, > 1, -ve$

27. The reference electrode is made from which of the following

[MP PET/PMT 1988]

(a) $ZnCl_2$
(b) $CuSO_4$
(c) Hg_2Cl_2
(d) $HgCl_2$

28. The charge over anode in a galvanic cell is

(a) Negative
(b) Positive
(c) No charge
(d) Sometimes negative and sometimes positive

29. The standard electrode potential for the two electrode A^+/A and B^+/B are respectively 0.5 V and 0.75 V. The emf of the given cell

$A \mid A^+(a=1) \mid\mid B^+(a=1) \mid B$ will be

(a) 1.25 V
(b) – 1.25 V
(c) – 0.25 V
(d) 0.25 V

30. The standard reduction potential for Li^+/Li; Zn^{2+}/Zn; H^+/H_2 and Ag^+/Ag is $-3.05, -0.762, 0.00$ and $+0.80\ V$. Which of the following has highest reducing capacity **[MP PMT 1992]**

(a) Ag (b) H_2

(c) Zn (d) Li

31. If an iron rod is dipped in $CuSO_4$ solution **[MADT Bihar 1984]**

(a) Blue colour of the solution turns green

(b) Brown layer is deposited on iron rod

(c) No change occurs in the colour of the solution

(d) Blue colour of the solution vanishes

(e) None of the above

32. E^o values of Mg^{2+}/Mg is $-2.37V$, of Zn^{2+}/Zn is $-0.76V$ and Fe^{2+}/Fe is $-0.44\ V$. Which of the following statements is correct **[EAMCET 1989]**

(a) Zn will reduce Fe^{2+}

(b) Zn will reduce Mg^{2+}

(c) Mg oxidises Fe

(d) Zn oxidises Fe

33. The standard reduction potential for Fe^{2+}/Fe and Sn^{2+}/Sn electrodes are -0.44 and -0.14 volt respectively. For the given cell reaction $Fe^{2+} + Sn \rightarrow Fe + Sn^{2+}$, the standard EMF is **[IIT Screening 1990; MP PMT 2003]**

(a) + 0.30 *V* (b) – 0.58 *V*

(c) + 0.58 *V* (d) – 0.30 *V*

34. Electrode potential of Zn^{2+}/Zn is $-0.76\ V$ and that of Cu^{2+}/Cu is $+0.34V$. The *EMF* of the cell constructed between these two electrodes is **[EAMCET 1992; BHU 2001; CBSE PMT 2001; KCET 1990; MHCET 1999, 2003; Pb. CET 2002; AFMC 2001; Pb. PMT 2004]**

(a) 1.10 *V* (b) 0.42 *V*

(c) – 1.1*V* (d) – 0.42 *V*

35. *EMF* of a cell whose half cells are given below is

$$Mg^{2+} + 2e^- \rightarrow Mg(s);\ E = -2.37\,V$$

$$Cu^{2+} + 2e^- \rightarrow Cu(s);\ E = +0.33\,V$$

[EAMCET 1987; MP PET 1994; Pb. PMT 2000]

(a) – 2.03 *V* (b) 1.36 *V*

(c) 2.7 *V* (d) 2.03 *V*

36. A cell constructed by coupling a standard copper electrode and a standard magnesium electrode has *emf* of 2.7 *volts*. If the standard reduction potential of copper electrode is + 0.34 *volt* that of magnesium electrode is **[KCET 1989]**

(a) + 3.04 *volts* (b) – 3.04 *volts*

(c) + 2.36 *volts* (d) – 2.36 *volts*

37. When $E^o_{Ag^+/Ag} = 0.8$ *volt* and $E^o_{Zn^{2+}/Zn} = -0.76$ *volt*, which of the following is correct **[MP PMT 1994]**

(a) Ag^+ can be reduced by H_2

(b) Ag can oxidise H_2 into H^+

(c) Zn^{2+} can be reduced by H_2

(d) Ag can reduce Zn^{2+} ion

38. Adding powdered lead and iron to a solution that is 1.0 *M* in both Pb^{2+} and Fe^{2+} ions, would result a reaction, in which **[CPMT 1987]**

(a) More iron and Pb^{2+} ions are formed

(b) More lead and Fe^{2+} ions are formed

(c) Concentration of both Pb^{2+} and Fe^{2+} ions increases

(d) There is no net change

39. Given standard electrode potentials

$$Fe^{++} + 2e^- \rightarrow Fe;\quad E^o = -0.440\ V$$

$$Fe^{+++} + 3e^- \rightarrow Fe;\quad E^o = -0.036\ V$$

The standard electrode potential (E^o) for $Fe^{+++} + e^- \rightarrow Fe^{++}$ is **[AIIMS 1982]**

(a) – 0.476 *V* (b) – 0.404 *V*

(c) + 0.404 *V* (d) + 0.771 *V*

40. Reduction potential of four elements P, Q, R, S is $-2.90, +0.34, +1.20$ and -0.76. Reactivity decreases in the order **[MP PET 1989; UPSEAT 2001]**

(a) $P > Q > R > S$ (b) $Q > P > R > S$

(c) $R > Q > S > P$ (d) $P > S > Q > R$

41. Which of the following metal can deposit copper from copper sulphate solution **[CPMT 1983; MP PMT 1989]**

(a) Mercury (b) Iron

(c) Gold (d) Platinum

42. Standard electrode potential of Ag^+/Ag and Cu^+/Cu is $+0.80V$ and $+0.34V$ respectively. these electrodes are joint together by salt bridge if **[AMU 2002]**

(a) Copper electrode is work like cathode, then E^o_{cell} is $+0.45V$

(b) Silver electrode is work like anode then E^o_{cell} is $-0.34V$

(c) Copper electrode is work like anode then E^o_{cell} is $+0.46V$

(d) Silver electrode is work like cathode then E^o_{cell} is $-0.34V$

(e) Silver electrode is work like anode then E^o_{cell} will be $+1.14V$

43. The reaction is spontaneous if the cell potential is **[MP PET 1999]**

(a) Positive (b) Negative

(c) Zero (d) Infinite

44. Which substance eliminates bromine from KBr solution **[IIT 1981]**

(a) I_2 (b) Cl_2

(c) HI (d) SO_2

45. A standard hydrogen electrode has zero electrode potential because **[IIT 1997]**

(a) Hydrogen is easiest to oxidise

(b) The electrode potential is assumed to be zero

(c) Hydrogen atom has only one electron

(d) Hydrogen is the lightest element

46. In the electrochemical cell

$H_2(g) 1\, atm | H^+(1M) || Cu^{2+}(1M) | Cu(s)$

Which one of the following statements is true **[EAMCET 1997]**

(a) H_2 is cathode; Cu is anode

(b) Oxidation occurs at Cu electrode

(c) Reduction occurs at H_2 electrode

(d) H_2 is anode; Cu is cathode

47. Expression representing the cell potential $(E\ cell)$

(a) $E_{cathode} + E_{anode}$ (b) $E_{anode} - E_{cathode}$

(c) $E_{cathode} - E_{anode}$ (d) $E_{left} - E_{right}$

48. Iron displaces copper from its salt solution, because **[MP PMT 1996]**

(a) Atomic number of iron is less than that of copper

(b) The standard reduction potential of iron is less than that of copper

(c) The standard reduction potential of iron is more than that of copper

(d) The iron salt is more soluble in water than the copper salt

49. (i) Copper metal dissolves in 1*M* silver nitrate solution and crystals of silver metal get deposited.

(ii) Silver metal does not react with 1 *M* zinc nitrate solution

(iii) Zinc metal dissolves in 1*M* copper sulphate solution and copper metal gets deposited

Hence the order of decreasing strength of the three metals as reducing agents will be

(a) $Cu > Ag > Zn$ (b) $Ag > Cu > Zn$

(c) $Zn > Cu > Ag$ (d) $Cu > Zn > Ag$

50. Standard electrode potentials of Zn and Fe are known to be (i) $-0.76\,V$ and (ii) $-0.44\,V$ respectively. How does it explain that galvanization prevents rusting of iron while zinc slowly dissolves away

(a) Since (i) is less than (ii), zinc becomes the cathode and iron the anode

(b) Since (i) is less than (ii), zinc becomes the anode and iron the cathode

(c) Since (i) is more than (ii), zinc becomes the anode and iron the cathode

(d) Since (i) is more than (ii), zinc becomes the cathode and iron the anode

51. Amongst the following electrodes the one with zero electrode potential is **[MP PMT 1997]**

(a) Calomel electrode

(b) Standard hydrogen electrode

(c) Glass electrode

(d) Gas electrode

52. Which of the following is correct expression for electrode potential of a cell **[MP PMT 1997]**

(a) $E = E^o - \frac{RT}{nF} \ln \frac{[\text{product}]}{[\text{reactant}]}$

(b) $E = E^o + \frac{RT}{F} \ln \frac{[\text{product}]}{[\text{reactant}]}$

(c) $E = E^o - \frac{RT}{nF} \ln \frac{[\text{reactant}]}{[\text{product}]}$

(d) $E = -\frac{RT}{F} \ln \frac{[\text{product}]}{[\text{reactant}]}$

53. Calculate standard free energy change for the reaction $\frac{1}{2}Cu(s) + \frac{1}{2}Cl_2(g) \rightleftharpoons \frac{1}{2}Cu^{2+} + Cl^-$ taking place at 25^oC in a cell whose standard e.m.f. is 1.02 *volts* **[MP PMT 1997]**

(a) – 98430 *J* (b) 98430 *J*

(c) 96500 *J* (d) – 49215 *J*

54. In which cell the free energy of a chemical reaction is directly converted into electricity ? **[MP PET/PMT 1998]**

(a) Leclanche cell (b) Concentration cell

(c) Fuel cell (d) Lead storage battery

55. Nernst equation is related with

(a) The electrode potential and concentration of ions in the solution

(b) Equilibrium constant and concentration of ions

(c) Free energy change and E.M.F. of the cell

(d) None of these

56. The standard reduction potentials of 4 elements are given below. Which of the following will be the most suitable reducing agent

I = – 3.04 *V*, II = – 1.90 V, III = 0 *V*, IV = 1.90 *V*

[CPMT 1999]

(a) I (b) II

(c) III (d) IV

57. Electrode potential data are given below :

$Fe^{3+}(aq) + e^- \rightarrow Fe^{-1}(aq); E^o = +0.77V$

$Al^{3+}(aq) + 3e^- \rightarrow Al(s); E^o = -1.66V$

$Br_2(aq) + 2e^- \rightarrow 2Br^-(aq); E^o = +1.08V$

Based on the data given above, reducing power of Fe^{2+}, Al and Br^- will increase in the order **[Pb. PMT 1998]**

(a) $Br^- < Fe^{2+} < Al$ (b) $Fe^{2+} < Al < Br^-$

(c) $Al < Br^- < Fe^{2+}$ (d) $Al < Fe^{2+} < Br^-$

58. The standard electrode potential (E^o) for OCl^- / Cl^- and $Cl^- / \frac{1}{2}Cl_2$ respectively are $0.94V$ and $-1.36V$. The E^o value for $OCl^- / \frac{1}{2}Cl_2$ will be **[KCET 1996]**

(a) $-0.42V$ (b) $-2.20V$

(c) $0.52V$ (d) $1.04V$

59. If the reduction potential is more, then **[CPMT 1996]**

(a) It is easily oxidised

(b) It is easily reduced

(c) It acts as oxidising agent

(d) It has redox nature

60. One of the following is false for Hg **[BHU 1998]**

(a) It can evolve hydrogen from H_2S

(b) It is a metal

(c) It has high specific heat

(d) It is less reactive than hydrogen

61. E^o for the cell $Zn \mid Zn^{2+}(aq) \mid\mid Cu^{2+}(aq) \mid Cu$ is $1.10V$ at 25^oC, the equilibrium constant for the reaction $Zn + Cu^{2+}(aq) \rightleftharpoons Cu + Zn^{2+}(aq)$ is of the order of

[CBSE PMT 1997]

(a) 10^{-28} (b) 10^{-37}

(c) 10^{+18} (d) 10^{+17}

62. Standard reduction potentials at 25^oC of $Li^+ \mid Li, Ba^{2+} \mid Ba, Na^+ \mid Na$ and $Mg^{2+} \mid Mg$ are $-3.05, -2.90, -2.71$ and -2.37 *volt* respectively. Which one of the following is the strongest oxidising agent

[CBSE PMT 1994; JIPMER 2002]

(a) Na^+ (b) Li^+

(c) Ba^{2+} (d) Mg^{2+}

63. Which of the following displaces Br_2 from an aqueous solution containing bromide ions

[CBSE PMT 1994; JIPMER (Med.) 2002]

(a) Cl_2 (b) Cl^-

(c) I_2 (d) I_3^-

64. For the cell reaction

$Cu^{2+}(C_1 aq) + Zn(s) = Zn^{2+}(C_2 aq) + Cu(s)$

of an electrochemical cell, the change in free energy at a given temperature is a function of

[CBSE PMT 1998]

(a) ln (C_1) (b) ln (C_2)

(c) ln $(C_1 + C_2)$ (d) ln (C_2 / C_1)

65. The e.m.f. of the cell in which the following reaction $Zn(s) + Ni^{2+}(a = 1.0) \rightleftharpoons Zn^{2+}(a = 10) + Ni(s)$ occurs, is found to be $0.5105V$ at $298K$. The standard e.m.f. of the cell is

[Roorkee Qualifying 1998]

(a) 0.5400 (b) 0.4810 *V*

(c) 0.5696 *V* (d) – 0.5105 *V*

66. For the redox reaction

$Zn(s) + Cu^{2+}(0.1M) \rightarrow Zn^{2+}(1M) + Cu(s)$

taking place in a cell, E^o_{cell} is 1.10 *volt*. E_{cell} for the cell will be $\left(2.303\frac{RT}{F} = 0.0591\right)$

[AIEEE 2003]

(a) 2.14 *volt* (b) 1.80 *volt*

(c) 1.07 *volt* (d) 0.82 *volt*

67. The *emf* of a Daniel cell at 298*K* is E_1 $Zn \mid \underset{(0.01\,M)}{ZnSO_4} \mid\mid \underset{(1.0\,M)}{CuSO_4} \mid Cu$ when the concentration of $ZnSO_4$ is 1.0 *M* and that of $CuSO_4$ is 0.01 *M*, the *emf* changed to E_2. What is the relationship between E_1 and E_2

[CBSE PMT 2003]

(a) $E_2 = 0 \neq E_1$ (b) $E_1 > E_2$

(c) $E_1 < E_2$ (d) $E_1 = E_2$

68. The oxidation potentials of following half-cell reactions are given $Zn \rightarrow Zn^{2+} + 2e^-; E^o = 0.76\ V$, $Fe \rightarrow Fe^{2+} + 2e^-; E^o = 0.44\ V$ what will be the *emf* of cell, whose cell-reaction is

$Fe^{2+}(aq) + Zn \rightarrow Zn^{2+}(aq) + Fe$

[MP PMT 2003]

(a) – 1.20 *V* (b) + 0.32 *V*

(c) – 0.32 *V* (d) + 1.20 *V*

69. The E^0 for half cells Fe/Fe^{2+} and Cu/Cu^{2+} are – 0.44 *V* and + 0.32 *V* respectively. Then **[MP PMT 2003]**

(a) Cu^{2+} oxidises Fe (b) Cu^{2+} oxidises Fe^{2+}

(c) Cu oxidises Fe^{2+} (d) Cu reduces Fe^{2+}

70. What is E^0 for electrode represented by $Pt, O_2(1\,atm)/2H^+(\text{Im})$ **[JIPMER 1997]**

(a) Unpredictable (b) Zero

(c) 0.018 *V* (d) 0.118 *V*

71. The cell potential of a cell in operation is

(a) Zero (b) Positive

(c) Negative (d) None of the above

72. Which of the following is displaced by Fe **[Roorkee 1995]**

(a) Ag (b) Hg

(c) Zn (d) Na

73. The standard electrode potential of the half cells are given below $Zn^{2+} + 2e^- \rightarrow Zn; E = -7.62\ V$, $Fe^{2+} + 2e^- \rightarrow Fe; E = -7.81\ V$

The *emf* of the cell $Fe^{2+} + Zn \rightarrow Zn^{2+} + Fe$ is **[CPMT 2003]**

(a) 1.54 *V* (b) – 1.54 *V*

(c) – 0.19 *V* (d) + 0.19 *V*

74. $Zn^{2+} + 2e^- \rightarrow Zn(s); E^o = -0.76$,
$Fe^{3+} + e^- \rightarrow Fe^{2+}; E^o = -0.77$,
$Cr^{3+} + 3e^- \rightarrow Cr; E^o = -0.79$,
$H^+ + 2e^- \rightarrow 1/2H_2; E^o = 0.00$

Strongest reducing agent is **[BHU 2003]**

(a) Fe^{2+} (b) Zn

(c) Cr (d) H_2

75. Standard reduction electrode potentials of three metals *A*, *B* and *C* are respectively + 0.5*V*, – 3.0*V* and – 1.2 *V*. The reducing powers of these metals are **[IIT 1998; AIEEE 2003]**

(a) *B* > *C* > *A* (b) *A* > *B* > *C*

(c) *C* > *B* > *A* (d) *A* > *C* > *B*

76. For a cell reaction involving a two-electron change, the standard *emf* of the cell is found to be 0.295 *V* at 25^oC. The equilibrium constant of the reaction at 25^oC will be

[Roorkee 1999; AIEEE 2003; CBSE PMT 2004]

(a) 1×10^{-10} (b) 29.5×10^{-2}

(c) 10 (d) 1×10^{10}

77. For the electrochemical cell, $M | M^+ || X^- | X$, $E^o(M^+/M)$ = 0.44 *V* and $E^o(X/X^-)$ = 0.33 *V*. From this data one can deduce that

[IIT-JEE (Screening) 2000]

(a) $M + X \rightarrow M^+ + X^-$ is the spontaneous reaction

(b) $M^+ + X^- \rightarrow M + X$ is the spontaneous reaction

(c) E_{cell} = 0.77 *V*

(d) E_{cell} = – 0.77 *V*

78. The standard potential at 25^oC for the following half reactions are given against them

$Zn^{2+} + 2e \rightarrow Zn, E^o = -0.762V$
$Mg^{2+} + 2e \rightarrow Mg, E^o = -2.37V$

When zinc dust is added to the solution of $MgCl_2$

[UPSEAT 2001]

(a) $ZnCl_2$ is formed

(b) *Zinc* dissolves in the solution

(c) No reaction takes place

(d) Mg is precipitated

79. $KMnO_4$ acts as an oxidising agent in the neutral medium and gets reduced to MnO_2. The equivalent weight of $KMnO_4$ in neutral medium **[AMU 2001]**

(a) *mol. wt*/2 (b) *mol.wt*/3

(c) *mol. wt*/4 (d) *mol .wt*/7

80. Which of the following condition will increase the voltage of the cell, represented by the equation $Cu_{(s)} + 2Ag^+_{(aq)} \rightarrow Cu^{2+}_{(aq)} + 2Ag_{(s)}$ **[CBSE PMT 2001]**

(a) Increase in the concentration of Ag^+ ion

(b) Increase in the concentration of Cu^+ ion

(c) Increase in the dimension of silver electrode

(d) Increase in the dimension of copper electrode

81. Which will increase the voltage of the cell $Sn_{(s)} + 2Ag^+_{(aq)} \rightarrow Sn^{2+}_{(aq)} + 2Ag_{(s)}$ **[DPMT 2001]**

(a) Increase in the concentration of Ag^+ ions

(b) Increase in the concentration of Sn^{2+} ions

(c) Increase in size of the silver rod

(d) None of these

82. The mass of the proton is 1840 times that of electron, its potential difference is *V*. The kinetic energy of proton is

[DCE 2001]

(a) 1840 *KeV* (b) 1 *KeV*

(c) $\frac{1}{1840}$ *KeV*	(d) 920 *KeV*

83. What will be the *emf* for the given cell $Pt\,|\,H_2(P_1)\,|\,H^+{}_{(aq)}\,||\,H_2(P_2)\,|\,Pt$ **[AIEEE 2002]**

(a) $\frac{RT}{f}\log\frac{P_1}{P_2}$	(b) $\frac{RT}{2f}\log\frac{P_1}{P_2}$

(c) $\frac{RT}{f}\log\frac{P_2}{P_1}$	(d) None of these

84. What is the potential of a cell containing two hydrogen electrodes the negative one in contact with 10^{-8} *M* H^+ and positive one in contact with 0.025 *M* H^+ **[MP PMT 2000]**

(a) 0.18 *V*	(b) 0.28 *V*

(c) 0.38 *V*	(d) 0.48 *V*

85. Will $Fe_{(s)}$ be oxidised to Fe^{2+} by the reaction with 1 *M HCl* (E^o for Fe/Fe^{2+} = + 0.44 *V*) **[Pb. PMT 2000]**

(a) Yes	(b) No

(c) May be	(d) Can't say

86. *EMF* of a cell in terms of reduction potential of its left and right electrodes is **[AIEEE 2002]**

(a) $E = E_{left} - E_{right}$	(b) $E = E_{left} + E_{right}$

(c) $E = E_{right} - E_{left}$	(d) $E = -(E_{right} + E_{left})$

87. Arrange the following in the order of their decreasing electrode potential *Mg*, *K*, *Ba*, *Ca* **[JIPMER 2002]**

(a) K, Ba, Ca, Mg	(b) Ca, Mg, K, Ba

(c) Ba, Ca, K, Mg	(d) Mg, Ca, Ba, K

88. Which of the following has highest electrode potential **[Pb. PMT 2000]**

(a) Li	(b) Cu

(c) Au	(d) Al

89. The cell reaction of a cell is

$$Mg_{(s)} + Cu^{2+}(aq) \rightarrow Cu_{(s)} + Mg^{2+}(aq)$$

If the standard reduction potentials of Mg and Cu are -2.37 and $+0.34\,V$ respectively. The *emf* of the cell is

[EAMCET 1995; JIPMER (Med.) 2001; AFMC 2002; CBSE PMT 2002]

(a) 2.03 *V*	(b) – 2.03 *V*

(c) + 2.71 *V*	(d) – 2.71 *V*

90. The element which can displace three other halogens from their compound is **[EAMCET 1998]**

(a) Cl	(b) F

(c) Br	(d) I

91. Which of the following has been universally accepted as a reference electrode at all temperatures and has been assigned a value of zero volt **[AIIMS 1998]**

(a) Graphite electrode

(b) Copper electrode

(c) Platinum electrode

(d) Standard hydrogen electrode

92. Aluminium is more reactive than Fe. But Al is less easily corroded than iron because **[DCE 1999]**

(a) *Al* is noble metal

(b) Iron forms both mono and divalent ions

(c) Oxygen forms a protective oxide layer

(d) *Fe* undergoes reaction easily with H_2O

93. Zinc displaces copper from the solution of its salt because **[MP PET 1995]**

(a) Atomic number of zinc is more than that of copper

(b) Zinc salt is more soluble in water than the copper salt

(c) Gibbs free energy of zinc is less than that of copper

(d) Zinc is placed higher than copper in electro-chemical series

94. An electrochemical cell is set up as follows

$Pt(H_2, 1\,atm)/0.1\,M\,HCl$

|| 0.1 *M* acetic acid /($H_2, 1\,atm$) *Pt*

E.M.F. of this cell will not be zero because **[CBSE PMT 1995]**

(a) The pH of 0.1 *M HCl* and 0.1 *M* acetic acid is not the same

(b) Acids used in two compartments are different

(c) E.M.F. of a cell depends on the molarities of acids used

(d) The temperature is constant

95. Cu^+ ion is not stable in aqueous solution because of disproportionation reaction. E^o value for disproportionation of Cu^+ is

(Given $E^o_{Cu^{2+}/Cu^+} = 0.15$, $E^o_{Cu^{2+}/Cu} = 0.34V$) **[IIT 1995]**

(a) – 0.49 *V*	(b) 0.49 *V*

(c) – 0.38 *V*	(d) 0.38 *V*

96. E^o of a cell $aA + bB \rightarrow cC + dD$ is **[CPMT 1997]**

(a) $-\frac{RT}{nF}\log\frac{[C]^c[D]^d}{[A]^a[B]^b}$ (b) $-RT\log\frac{[a]^A[b]^B}{[a]^C[d]^D}$

(c) $-\frac{RT}{nF}\log\frac{[C]^c[d]^D}{[A]^a[B]^b}$ (d) $-\frac{RT}{nF}\log\frac{[C]^c[d]^D}{[a]^A[B]^b}$

97. In the experiment set up for the measurement of *EMF* of a half cell using a reference electrode and a salt bridge, when the salt bridge is removed, the voltage **[NCERT 1984; CPMT 1985]**

(a) Does not change

(b) Decreases to half the value

(c) Increase to maximum

(d) Drops to zero

98. Electrode potentials of five elements A, B, C, D and E are respectively – 1.36 , – 0.32, 0, – 1.26 and – 0.42. The reactivity order of these elements are in the order of

[MP PMT 1995]

(a) *A, D, E, B* and *C* (b) *C, B, E, D* and *A*

(c) *B, D, E, A* and *C* (d) *C, A, E, D* and *B*

99. What is wrongly stated about electrochemical series **[DCE 1999]**

(a) It is the representation of element in order of increasing or decreasing standard electrode reductional potential

(b) It does not compare the relative reactivity of metals

(c) It compares relative strengths of oxidising agents

(d) H_2 is centrally placed element

100. Which of the following statements is true for fuel cells **[KCET (Med.) 1999; AFMC 2000]**

(a) They are more efficient

(b) They are free from pollution

(c) They run till reactants are active

(d) All of these

101. What is the potential of a half-cell consisting of zinc electrode in 0.01*m* $ZnSO_4$ solution at 258^oC $(E^o = 0.763V)$

[AIIMS 2000; BHU 2000]

(a) 0.8221 *V* (b) 8.221 *V*

(c) 0.5282 *V* (d) 9.232 *V*

102. The *emf* of a galvanic cell, with electrode potentials of silver = +0.80*V* and that of copper = + 0.34 *V*, is **[AIIMS 1999]**

(a) – 1.1 *V* (b) + 1.1 *V*

(c) + 0.46 *V* (d) + 0.76 *V*

103. Copper cannot replace..... from solution **[DPMT 2002]**

(a) Fe (b) Au

(c) Hg (d) Ag

104. The strongest reducing agent of the alkali metal is **[CBSE PMT 2000]**

(a) Li (b) Na

(c) K (d) Cs

105. Which of the following is the most electropositive element

[Pb. PMT 2000]

(a) Carbon (b) Calcium

(c) Chlorine (d) Potassium

106. The metal that forms a self protecting film of oxide to prevent corrosion, is **[BHU 1999]**

(a) Cu (b) Al

(c) Na (d) Au

107. In a cell that utilises the reaction $Zn_{(s)} + 2H^+(aq) \rightarrow Zn^{2+}(aq) + H_{2(g)}$ addition of H_2SO_4 to cathode compartment, will **[AIEEE 2004]**

(a) Increase the *E* and shift equilibrium to the right

(b) Lower the *E* and shift equilibrium to the right

(c) Lower the *E* and shift equilibrium to the left

(d) Increase the *E* and shift equilibrium to the left

108. For the electrochemical cell, $M\,|\,M^+\,||\,X^-\,|\,X$, $E^\circ(M^+\,|\,M) = 0.44\ V$ $E^\circ(X\,|\,X^-) = 0.33\ V$ From this data, one can deduce that

[Pb.CET 2004]

(a) $E^\circ_{cell} = -0.77V$

(b) $M^+ + X^- \rightarrow M + X$ is the spontaneous reaction

(c) $M + X \rightarrow M^+ + X^-$ is the spontaneous reaction

(d) $E^\circ_{cell} = .77\ V$

109. The standard *e.m.f.* of a call, involving one electron change is found to be $0.591\ V$ at 25°*C*. The equilibrium constant of the reaction is ($F = 96{,}500\ C\ mol^{-1};\ R = 8.314\ JK^{-1}mol^{-1}$)

[AIEEE 2004]

(a) 1.0×10^{10} (b) 1.0×10^{5}

(c) 1.0×10^{1} (d) 1.0×10^{30}

110. Standard electrode potential of cell $H_2\,|\,H^+\,||\,Ag^+\,|\,Ag$ is

[AIEEE 2004]

(a) 0.8 *V* (b) – 0.8 *V*

(c) – 1.2 *V* (d) 1.2 *V*

111. A galvanic cell with electrode potential of $'A' = +2.23\ V$ and $'B' = -1.43\ V$. The value of E°_{cell} is **[Pb.CET 2003]**

(a) 3.66 *V* (b) 0.80 *V*

(c) – 0.80 *V* (d) – 3.66 *V*

112. The *e.m.f.* of a cell whose half cells are given below is

$Mg^{2+} + 2e^- \rightarrow Mg(s)\ E^\circ = -2.37\ V$

$Cu^{2+} + 2e^- \rightarrow Cu(s)\ E^\circ = +0.34\ V$ **[Pb.CET 2001]**

(a) + 1.36 *V* (b) + 2.71 *V*

(c) + 2.17 *V* (d) – 3.01 *V*

113. For the cell reaction, $2Ce^{4+} + Co \rightarrow 2Ce^{3+} + Co^{2+}$ E°_{cell} is 1.89 *V*. If $E^\circ_{Ce^{4+}/Ce^{3+}}$ **[Pb.CET 2000]**

(a) – 1.64 *V* (b) + 1.64 *V*

(c) – 2.08 *V* (d) + 2.17 *V*

114. If the ΔG of a cell reaction $AgCl + e^- \rightarrow Ag + Cl^-$ is $-21.20\ KJ$; the standard *e.m.f.,* of cell is **[MP PMT 2004]**

(a) 0.229 *V* (b) 0.220 *V*

(c) – 0.220 *V* (d) – 0.110 *V*

115. The *e.m.f.* of the cell $Ag \mid Ag^+(0.1M) \mid\mid Ag^+(1M) \mid Ag$ at 298 *K* is **[DCE 2003]**

(a) 0.0059 *V* (b) 0.059 *V*

(c) 5.9 *V* (d) 0.59 *V*

116. The *e.m.f.* of the cell

$Zn \mid Zn^{2+}(0.01M) \mid\mid Fe^{2+}(0.001M) \mid Fe$ at 298 *K*

is 0.2905 then the value of equilibrium for the cell reaction is **[IIT-JEE Screening 2004]**

(a) $\frac{0.32}{e^{0.0295}}$ (b) $\frac{0.32}{10^{0.0295}}$

(c) $\frac{0.26}{10^{0.0295}}$ (d) $\frac{0.32}{10^{0.0591}}$

117. Aluminium displaces hydrogen from dilute *HCl* whereas silver does not. The *e.m.f.* of a cell prepared by combining Al / Al^{3+} and Ag / Ag^+ is 2.46 *V*. The reduction potential of silver electrode is $+0.80\ V$. The reduction potential of aluminium electrode is **[KCET 2004]**

(a) $+1.66\ V$ (b) $-3.26\ V$

(c) $3.26\ V$ (d) $-1.66\ V$

118. Consider the following E^0 values :

$E^0_{Fe^{3+}/Fe^{2+}} = +0.77\ V$

$E^0_{Sn^{2+}/Sn} = -0.14\ V$

Under standard conditions the potential for the reaction

$Sn_{(s)} + 2Fe^{3+}(aq) \rightarrow 2Fe^{2+}(sq) + Sn^{2+}(aq)$ is **[AIEEE 2004]**

(a) 0.91 *V* (b) 1.40 *V*

(c) 1.68 *V* (d) 0.63 *V*

119. $Cr_2O_7^{2-} + I^- \rightarrow I_2 + Cr^{3+}$

$E^0_{cell} = 0.79\ V$

$E^0_{Cr_2O_7^{2-}} = 1.33\ V,\ E^0_{I_2}$ is

[BVP 2004]

(a) $-0.10\ V$ (b) $+0.18\ V$

(c) $-0.54\ V$ (d) $0.54\ V$

120. $Zn(s) + Cl_2(1\ \text{atm}) \rightarrow Zn^{2+} + 2Cl^-$. E^0_{cell} of the cell is 2.12 *V*. To increase *E* **[BVP 2004]**

(a) $[Zn^{2+}]$ should be increased

(b) $[Zn^{2+}]$ should be decreased

(c) $[Cl^-]$ should be decreased

(d) P_{Cl_2} should be decreased

121. The $E^0_{M^{3+}/M^{2+}}$ values for Cr, Mn, Fe and Co are $-0.41, +1.57, +0.77$ and $+1.97\ V$ respectively. For which one of these metals the change in oxidation state from $+2$ to $+3$ is easiest **[AIEEE 2004]**

(a) *Fe* (b) *Mn*

(c) *Cr* (d) *Co*

122. The rusting of iron takes place as follows

$2H^+ + 2e^- + \frac{1}{2}O_2 \rightarrow H_2O(l)$;

$E^\circ = +1.23\ V$

$Fe^{2+} + 2e^- \rightarrow Fe(s)$; $E^\circ = -0.44\ V$

Calculate ΔG° for the net process **[IIT 2005]**

(a) –322 *kJ mol*$^{-1}$ (b) –161 *kJ mol*$^{-1}$

(c) –152 *kJ mol*$^{-1}$ (d) –76 *kJ mol*$^{-1}$

123. When an acid cell is charged, then **[AFMC 2005]**

(a) Voltage of cell increases

(b) Electrolyte of cell dilutes

(c) Resistance of cell increases

(d) None of these

124. The standard electrode potential is measured by **[KCET 2005]**

(a) Electrometer (b) Voltmeter

(c) Pyrometer (d) Galvanometer

125. Aluminium displaces hydrogen from acids but copper does not. A galvanic cell prepared by combining Cu / Cu^{2+} and Al / Al^{3+} has an *e.m.f.* of 2.0 *V* at 298 *K*. If the potential of copper electrode is + 0.34 *V*, that of aluminium is **[CPMT 2001; KCET 2001]**

(a) + 1.66 *V* (b) – 1.66 *V*
(c) + 2.34 *V* (d) – 2.3 *V*

126. If the standard electrode potential of Cu^{2+} / Cu electrode is 0.34*V*, what is the electrode potential of 0.01*M* concentration of Cu^{2+} $(T = 298 K)$ **[EAMCET 2003]**

(a) 0.399 *V* (b) 0.281 *V*
(c) 0.222 *V* (d) 0.176 *V*

127. Calculate the electrode potential at $298^o K$ for $Zn | Zn^{++}$ electrode in which the activity of zinc ions is 0.001 *M* and $E^0_{Zn/Zn^{++}}$ is –0.74 *volts* **[AMU 2002]**

(a) 0. 38 *volts* (b) 0.83 *volts*
(c) 0.40 *volts* (d) 0.45 *volts*

128. Which of the following expression is correct **[Orissa JEE 2005]**

(a) $\Delta G^o = -nFE^o_{cell}$ (b) $\Delta G^o = +nFE^o_{cell}$
(c) $\Delta G^o = -2.303RT\ nFE^o_{cell}$ (d) $\Delta G^o = -nF \log K_C$

129. For the feasibility of a redox reaction in a cell, the e.m.f. should be **[J & K 2002]**

(a) Positive (b) Fixed
(c) Zero (d) Negative

Corrosion

1. Corrosion is basically a **[Kerala (Med.) 2002]**

(a) Altered reaction in presence of H_2O
(b) Electrochemical phenomenon
(c) Interaction
(d) Union between light metal and heavy metal

2. Rusting of iron is catalysed by which of the following **[MNR 1990; UPSEAT 2001]**

(a) Fe (b) O_2
(c) Zn (d) H^+

3. Which of the following is a highly corrosive salt **[AFMC 2005]**

(a) $FeCl_2$ (b) $PbCl_2$
(c) Hg_2Cl_2 (d) $HgCl_2$

4. Corrosion of iron is essentially an electrochemical phenomenon where the cell reactions are **[KCET 2005]**

(a) Fe is oxidised to Fe^{2+} and dissolved oxygen in water is reduced to $\overset{-}{O}H$

(b) Fe is oxidised to Fe^{3+} and H_2O is reduced to O_2^{2-}

(c) Fe is oxidised to Fe^{2+} and H_2O is reduced to O_2^-

(d) Fe is oxidised to Fe^{2+} and H_2O is reduced to O_2

Critical Thinking

Objective Questions

1. The limiting molar conductivities Λ^0 for *NaCl, KBr* and *KCl* are 126, 152 and 150 $S\ cm^2 mol^{-1}$ respectively. The Λ^0 for *NaBr* is **[AIEEE 2004]**

(a) $278\ S\ cm^2 mol^{-1}$ (b) $176\ S\ cm^2 mol^{-1}$
(c) $128\ S\ cm^2 mol^{-1}$ (d) $302\ S\ cm^2 mol^{-1}$

2. On the basis of the electrochemical theory of aqueous corrosion, the reaction occurring at the cathode is **[MP PET 1994; UPSEAT 2001]**

(a) $O_{2(g)} + 4H^+_{(aq)} + 4e^- \to 2H_2O_{(l)}$
(b) $Fe_{(s)} \to Fe^{2+}_{(aq)} + 2e^-$
(c) $Fe^{2+}_{(aq)} \to Fe^{3+}_{(aq)} + e^-$
(d) $H_{2(g)} + 2OH^-_{(aq)} \to 2H_2O_{(l)} + 2e^-$

3. The reaction

$\frac{1}{2} H_2(g) + AgCl(s) \to H^+(aq) + Cl^-(aq) + Ag(s)$

occurs in the galvanic cell **[IIT 1985; AMU 2002; KCET 2003]**

(a) $Ag / AgCl(s) KCl\ (soln) \,||\, AgNO_3 (soln) / Ag$
(b) $Pt / H_2(g) HCl\ (soln) \,||\, AgNO_3 (soln) / Ag$
(c) $Pt / H_2(g) HCl\ (soln) \,||\, AgCl\ (s) / Ag$
(d) $Pt / H_2(g) KCl\ (soln) \,||\, AgCl\ (s) / Ag$

4. The standard reduction potential E^o for the half reactions are as

$Zn = Zn^{2+} + 2e^-;\ E^o = +0.76 V$

$Fe = Fe^{2+} + 2e^-;\ E^o = +0.41 V$

The *EMF* for cell reaction $Fe^{2+} + Zn \to Zn^{2+} + Fe$ is

[IIT 1988; CBSE PMT 1993, 96; BHU 1995, 2000; CPMT 2000; KCET 2000; AIIMS 2001; Orissa JEE 2002]

(a) $-0.35\,V$ (b) $+0.35\,V$
(c) $+1.17\,V$ (d) $-1.17\,V$

5. The number of electrons to balance the following equation $NO_3^- + 4H^+ + e^- \rightarrow 2H_2O + NO$ is **[IIT Screening 1991]**

(a) 5 (b) 4
(c) 3 (d) 2

6. The standard EMF for the given cell reaction $Zn + Cu^{2+} = Cu + Zn^{2+}$ is $1.10V$ at $25^{\circ}C$. The EMF for the cell reaction, when $0.1M\ Cu^{2+}$ and $0.1M\ Zn^{2+}$ solutions are used, at $25^{\circ}C$ is

[MNR 1994; AMU 1999; UPSEAT 2002]

(a) $1.10V$ (b) $0.110V$
(c) $-1.10V$ (d) $-0.110V$

7. A gas X at $1\,atm$ is bubbled through a solution containing a mixture of $1\,M\,Y^-$ and $1\,M\,Z^-$ at $25^{\circ}C$. If the reduction potential of $Z > Y > X$, then **[IIT 1999]**

(a) Y will oxidize X and not Z
(b) Y will oxidize Z and not X
(c) Y will oxidize both X and Z
(d) Y will reduce both X and Z

8. The oxidation potential of a hydrogen electrode at *pH* = 10 and $pH_1 = 1$ **[JIPMER 2000]**

(a) 0.059 *V* (b) 0.59 *V*
(c) 0.00 *V* (d) 0.51 *V*

9. The decomposition of hydrogen peroxide is an example of

[Roorkee 2000]

(a) Exothermic reaction (b) Endothermic reaction
(c) Negative catalysis (d) Auto-oxidation

10. Aluminium oxide may be electrolysed at 1000°C to furnish aluminium metal (At. Mass = 27 *amu*; 1 *Faraday* = 96,500 *Coulombs*). The cathode reaction is

$Al^{3} + 3e^- \rightarrow Al^{\circ}$

To prepare 5.12*kg* of aluminium metal by this method would require **[AIEEE 2005]**

(a) $5.49 \times 10^7\,C$ of electricity
(b) $1.83 \times 10^7\,C$ of electricity
(c) $5.49 \times 10^4\,C$ of electricity
(d) $5.49 \times 10^1\,C$ of electricity

11.

Electrolyte :	*KCl*	KNO_3	*HCl*	*NaOAc*	*NaCl*
$\Lambda^{\infty}(Scm^2mol^{-1})$:	149.9	145.0	426.2	91.0	126.

Calculate Λ^{∞}_{HOAc} using appropriate molar conductances of the electrolytes listed above at infinite dilution in H_2O at 25°*C* **[AIEEE 2005]**

(a) 517.2 (b) 552.7
(c) 390.7 (d) 217.5

12. The mass of carbon anode consumed (giving only carbondioxide) in the production of 270*kg* of aluminium metal from bauxite by the Hall process is **[CBSE PMT 2005]**

(a) 180*kg* (b) 270*kg*
(c) 540*kg* (d) 90*kg*

13. 4.5*g* of aluminium (at mass 27*amu*) is deposited at cathode from Al^{3+} solution by a certain quantity of electric charge. The volume of hydrogen produced at STP from H^+ ions in solution by the same quantity of electric charge will be

[CBSE PMT 2005]

(a) 22.4 *L* (b) 44.8 *L*
(c) 5.6 *L* (d) 11.2 *L*

14. What amount of Cl_2 gas liberated at anode, if 1 *amp*. current is passed for 30 *min*. from *NaCl* solution.

[BHU 2005]

(a) 0.66 moles (b) 0.33 moles
(c) 0.66 *g* (d) 0.33 *g*

Assertion & Reason

For AIIMS Aspirants

Read the assertion and reason carefully to mark the correct option out of the options given below :

(a) If both assertion and reason are true and the reason is the correct explanation of the assertion.
(b) If both assertion and reason are true but reason is not the correct explanation of the assertion.
(c) If assertion is true but reason is false.
(d) If the assertion and reason both are false.
(e) If assertion is false but reason is true.

1. Assertion : Sodium ions are discharged in preference to hydrogen ions at a mercury cathode.
Reason : The nature of the cathode can effect the order of discharge of ions.

2. Assertion : In electrolysis, the quantity of electricity needed for depositing 1 mole of silver is different from that required for 1 mole of copper.
Reason : The molecular weights of silver and copper are different

3. Assertion : Equivalent conductance of all electrolytes decreases with the increases in concentration.

Reason : Lesser number of ions are available per gram equivalent at higher concentration.

4. Assertion : Copper reacts with hydrochloric acid and liberates hydrogen from the solution of dilute hydrochloric acid.

Reason : Hydrogen is below copper in the electrochemical series.

5. Assertion : Copper liberates hydrogen from a solution of dil. HCl.

Reason : Hydrogen is below copper in the reactivity series.

6. Assertion : Zn metal is formed when a Cu plate in dipped in $ZnSO_4$ solution.

Reason : Cu being placed above Zn in electrochemical series.

7. Assertion : Electrical conductivity of copper increases with increase in temperature.

Reason : The electrical conductivity of metals is due to the motion of electrons.

8. Assertion : A small amount of acid or alkali is added before electrolysis of water.

Reason : Pure water is weak electrolyte.

9. Assertion : Copper reacts with HCl and liberates hydrogen.

Reason : Hydrogen is present above Cu in the reactivity series.

10. Assertion : K and Cs are used in photoelectric cells.

Reason : K and Cs emit electrons on exposure to light.

11. Assertion : A large dry cell has high *e.m.f.*

Reason : The *e.m.f.* of a dry cell is proportional to its size.

12. Assertion : The resistivity for a substance is its resistance when its is one meter long and its area of cross section is one square meter.

Reason : The *SI* uints of resistivity are ohm metre (Ωm) and ohm centimeter (Ωcm).

13. Assertion : When acidified zinc sulphate solution is electrolysed between zinc electrodes, it is zinc that is deposited at the cathode and hydrogen evolution does not take place.

Reason : The electrode potential of zinc is more negative than hydrogen as the overvoltage for the hydrogen as the evolution on zinc is quite large.

14. Assertion : If $\lambda^0_{Na^+} + \lambda^0_{Cl^-}$ are molar limiting conductivity of the sodium and chloride ions respectively, then the limiting molar conducting for sodium chloride is given by the equation: $\wedge^0_{NaCl} = \lambda^0_{Na^+} + \lambda^0_{Cl^-}$.

Reason : This is according to Kohlrausch law of independent migration of ions.

15. Assertion : One coulomb of electric charge deposits weight equal to the electrochemical equivalent of the substance.

Reason : One Faraday deposits one mole of the substance.

16. Assertion : Auric chloride $(AuCl_3)$ solution cannot be stored in a vessel made of copper, iron, nickel, chromium, zinc or tin.

Reason : Gold is a very precious metal.

17. Assertion : For a cell reaction $Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu(s)$; at the equilibrium, voltmeter gives zero reading.

Reason : At the equilibrium, there is no change in the concentration of Cu^{2+} and Zn^{2+} ions.

18. Assertion : A negative value of standard reduction potential means that reduction take place on this electrode with reference to standard hydrogen electrode.

Reason : The standard electrode potential of a half cell has a fixed value.

19. Assertion : Weston is a standard cell.

Reason : Its *e.m.f.* does not change with temperature.

20. Assertion : Galvanic cells containing hydrogen, methane, methanol etc. as fuels are called fuel cells.

Reason : They are designed to convert the energy of combustion of fuels directly into electrical energy.

21. Assertion : Zinc displaces copper from copper sulphate solution.

Reason : The E^0 of zinc is $-0.76\ V$ and that of copper is $+0.34\ V$.

22. Assertion : Identification of cathode and anode is done by the use of a thermometer.

Reason : Higher is the value of reduction potential, greater would be its reducing power.

23. Assertion : An electrochemical cell can be set up only if the redox reaction is spontaneous.

Reason : A reaction is spontaneous if free energy change is negative.

24. Assertion : Galvanised iron does not rust.

Reason : Zinc has a more negative electrode potential than iron. **[AIIMS 2005]**

25. Assertion : In an electrochemical cell anode and cathode are respectively negative and positive electrodes.

Reason : At anode oxidation takes place and at cathode reduction takes place.

26. Assertion : $Ni / Ni^{2+}(1.0M) || Au^{3+}(1.0M) | Au$, for this cell emf is 1.75 V if $E^o_{Au^{3+}/Au} = 1.50$ and $E^o_{Ni^{2+}/Ni} = 0.25V$.

Reason : Emf of the cell $= E^o_{cathode} - E^o_{anode}$.

27. Assertion : Salts like KCl, KNO_3 i.e., inert electrolytes are used in salt bridge.

Reason : An inert electrolyte can easily be filled in the U-tube.

28. Assertion : Emf and potential difference are same for cell.

Reason : Both gives the difference in electrode potential under any condition.

Answers

Electrolytes and Electrolysis

1	b	2	d	3	c	4	c	5	d
6	d	7	b	8	b	9	b	10	a
11	a	12	c	13	d	14	d	15	c
16	d	17	a	18	c	19	c	20	a
21	a	22	b	23	b	24	d	25	b
26	b	27	b	28	a	29	c	30	b
31	d	32	d	33	c	34	b	35	b
36	a	37	d	38	c	39	d	40	a
41	a								

Faraday's law of electrolysis

1	c	2	a	3	b	4	c	5	c
6	c	7	c	8	b	9	c	10	a
11	c	12	a	13	c	14	b	15	b
16	c	17	a	18	a	19	d	20	c
21	d	22	c	23	b	24	d	25	a
26	d	27	a	28	d	29	c	30	a
31	b	32	b	33	a	34	b	35	b
36	b	37	b	38	b	39	a	40	a
41	c	42	a	43	a	44	b	45	c
46	b	47	d	48	d	49	b	50	a
51	c	52	b	53	b	54	a	55	c
56	c	57	c	58	d	59	d	60	d
61	c	62	c	63	b	64	a	65	b
66	b	67	a	68	a	69	b	70	c
71	c	72	b	73	a	74	b	75	c
76	b	77	c	78	c	79	b	80	b
81	c	82	b	83	a	84	c	85	c
86	e	87	b	88	a	89	d	90	c
91	c	92	a	93	c	94	b		

Conductor and Conductance

1	b	2	b	3	d	4	d	5	a
6	b	7	b	8	a	9	b	10	d
11	a	12	b	13	b	14	b	15	b
16	d	17	b	18	d	19	b	20	c
21	b	22	a	23	c	24	d	25	a
26	b	27	d						

Cell constant and Electrochemical cells

1	d	2	d	3	d	4	b	5	b
6	a	7	c	8	c	9	b	10	b
11	c	12	c	13	a	14	a	15	d
16	c	17	c	18	a	19	b	20	b
21	b	22	b	23	a	24	b	25	c
26	a	27	c	28	a	29	b	30	c
31	a	32	b	33	c	34	b	35	d
36	b	37	c	38	d	39	b	40	d
41	a	42	d	43	c	44	a	45	d
46	a	47	d	48	b	49	c	50	c
51	b	52	d	53	c	54	a	55	c
56	d	57	b	58	a	59	a	60	c
61	a								

Electrode potential, E_{Cell}, Nernst equation and ECS

1	b	2	a	3	a	4	b	5	d

6	c	7	c	8	a	9	a	10	b
11	a	12	c	13	a	14	d	15	c
16	a	17	a	18	c	19	b	20	b
21	a	22	b	23	a	24	c	25	a
26	a	27	c	28	a	29	d	30	d
31	b	32	a	33	d	34	a	35	c
36	d	37	a	38	b	39	d	40	d
41	b	42	c	43	a	44	b	45	b
46	d	47	c	48	b	49	c	50	b
51	b	52	a	53	a	54	c	55	a
56	a	57	a	58	a	59	c	60	a
61	b	62	d	63	a	64	d	65	b
66	c	67	b	68	b	69	a	70	b
71	b	72	ab	73	c	74	c	75	a
76	d	77	b	78	c	79	b	80	a
81	a	82	b	83	b	84	c	85	a
86	c	87	a	88	c	89	c	90	b
91	d	92	c	93	d	94	a	95	d
96	a	97	d	98	a	99	b	100	d
101	a	102	c	103	a	104	a	105	d
106	b	107	a	108	b	109	a	110	a
111	a	112	b	113	b	114	b	115	b
116	b	117	d	118	a	119	d	120	b
121	c	122	a	123	a	124	b	125	b
126	b	127	b	128	a	129	a		

Corrosion

1	b	2	d	3	d	4	a		

Critical Thinking Questions

1	c	2	a	3	c	4	b	5	c
6	a	7	a	8	b	9	acd	10	a
11	c	12	d	13	c	14	c		

Assertion & Reason

1	a	2	b	3	a	4	d	5	d
6	d	7	e	8	a	9	e	10	a
11	d	12	b	13	a	14	a	15	c
16	b	17	a	18	e	19	a	20	a
21	a	22	d	23	b	24	a	25	a
26	a	27	c	28	d				

Answers and Solutions

Electrolytes and Electrolysis

1. (b) Sugar solution does not form ion; hence does not conduct electricity in solution.

3. (c) Strong electrolytes are almost completely ionised in polar solvent.

7. (b) The reduction potential of Mg is less than that of water $(E^o = -0.83V)$. Hence their ions in the aqueous solution cannot be reduced instead water will be reduced $2H_2O + 2e^- \rightarrow H_2 + 2OH^-$.

8. (b) HCl is an electrolyte.

9. (b) Water is reduced at the cathode and oxidized at the anode instead of Na^+ and SO_4^{2-}.

Cathode: $2H_2O + 2e^- \rightarrow H_2 + 2OH^-$

Anode : $H_2O \rightarrow 2H^+ + \frac{1}{2}O_2 + 2e^-$.

10. (a) In electrolysis process oxidation occurs at anode and reduction occurs at cathode.

11. (a) Because in it covalent bonding is present.

12. (c) According to Faraday's law.

13. (d) Impure metal made anode while pure metal made cathode.

14. (d) In electrolytic cell, cathode acts as source of electrons.

15. (c) $AgNO_3$ is an electrolyte.

17. (a) At cathode: $2H^+ + 2e \rightarrow H_2$,

At anode : $2OH^- \rightarrow H_2O + \frac{1}{2}O_2 + 2e$

18. (c) In between dilute H_2SO_4 and platinum electrode O_2 gas evolve at anode.

19. (c) When polar solvent added in to solid electrolyte than it is ionised.

20. (a) In fused $NaCl$ chloride ions are oxidized at anode and it is called oxidation.

21. (a) $w = zit, Q = it$.

22. (b) $2H^+ + 2e^- \rightarrow H_{2(g)}$ at cathode.

23. (b) $\underset{+1}{Na^+} + e^- \rightarrow \underset{0}{Na}$, means oxidation number is decreased so the reaction is reduction.

24. (d) Degree of dissociation of weak electrolyte increases on increasing temperature.

25. (b) Since discharge potential of water is greater than that of sodium so water is reduced at cathode instead of Na^+

Cathode: $H_2O + e^- \rightarrow \frac{1}{2}H_2 + OH^-$

Anode: $Cl^- \rightarrow \frac{1}{2}Cl_2 + e^-$.

26. (b) Because it does not have ions.

27. (b) $NaCl \rightleftharpoons Na^+ + Cl^-$.

28. (a) Cathode: $2H_2O + 2e^- \rightarrow H_2 + 2OH^-$

Anode : $H_2O \rightarrow 2H^+ + \frac{1}{2}O_2 + 2e^-$.

29. (c) Electrolysis use for electroplating and electrorefining.

32. (d) The degree of ionization depend upon the nature of the solute the size of the solute molecules and the concentration of the solution.

33. (c) $C_{12}H_{22}O_{11}$ is an non-electrolyte.

34. (b) On electrolysis molten ionic hydride liberate H_2 at the anode.

35. (b) During electrolysis cation discharged at cathode and anion discharged at anode.

36. (a) Calcium is produces when molten anhydrous calcium chloride is electrolysed.

37. (d) All metals conducts heat and electricity.

38. (c) $2Al + dil.H_2SO_4 \rightarrow Al_2SO_4 + H_2\uparrow$.

39. (d) Generally fussed potassium chloride flow the electric conductivity.

41. (a) The substances whose aqueous solutions allow the passage of electric current and are chemically decomposed, are termed electrolytes. Electrolytic substances are classified as strong or weak according to how readily they dissociate into conducting ions. Acetic acid is a weak electrolyte. Glucose, ethanol and urea are non-electrolytes.

Faraday's law of electrolysis

1. (c) $Ag^+ + e^- \rightarrow Ag;\ E_{Ag} = \frac{Atomic\ Mass}{1} = 108$

Number of faraday $= \frac{W_{Ag}}{E_{Ag}} = \frac{108}{108} = 1$.

2. (a) $W_{Ag} = \frac{E_{Ag} \times Q}{96500} = \frac{108 \times 9.65}{96500}$

$= 1.08 \times 10^{-2}\ gm = 10.8\ mg$

3. (b) $Fe^{2+} + 2e^- \rightarrow Fe;\ E_{Fe} = \frac{56}{2} = 28$

$W_{Fe} = E_{Fe}$ × Number of faraday $= 28 \times 3 = 84\ gm$.

4. (c)

$$W_{Ag} = \frac{E_{Ag} \times Q}{96500} = \frac{107.87 \times 965}{96500} = 1.0787\ gm.$$

5. (c) $Al^{3+} + 3e^- \rightarrow Al$

$$E_{Al} = \frac{27}{3} = 9$$

$$W_{Al} = E_{Al} \times \text{No. of faradays} = 9 \times 5 = 45\ gm$$

.

6. (c) *Cu* voltameter or *Cu* or *Ag* coulometer are used to detect the amount deposited on an electrode during passage of know charge through solution.

8. (b) $\frac{\text{Weight of } Cu}{\text{Weight of } H_2} = \frac{\text{Eq. weight of } Cu}{\text{Eq. weight of } H}$

$$\frac{\text{Weight of } Cu}{0.50} = \frac{63.6/2}{1}$$

$$\text{Weight of } Cu = 15.9\ gm.$$

9. (c) $Cu^{2+} + 2e^- \rightarrow Cu$

2 Faradays will deposit $= 1\ g\ atom\ of\ Cu = 63.5\ g$.

12. (a) At cathode; $Al^{3+} + 3e^- \rightarrow Al$

$$E_{Al} = \frac{27}{3} = 9$$

$$W_{Al} = E_{Al} \times \text{No. of faradays}$$

$$= 9 \times 0.1 = 0.9\ gm.$$

14. (b) $W = zit;$

$$W = \frac{32.69 \times 5 \times 60 \times 40}{96500} = 4.065\ gm.$$

15. (b) $m = Z \times 4 \times 120$; $M = Z \times 6 \times 40$

$$\frac{M}{m} = \frac{6 \times 40}{4 \times 120} = \frac{1}{2}; \quad M = m/2.$$

16. (c) $W_{\text{metal}} = \frac{E \times I \times t}{96500} = \frac{E \times 3 \times 50 \times 60}{96500}$

$$E = \frac{96500 \times w}{3 \times 50 \times 60} = \frac{96500 \times 1.8}{3 \times 50 \times 60} = 19.3.$$

17. (a) $Al \rightarrow Al^{3+} + 3e^-$.

The charged obtained is $3 \times 96500C$.

18. (a)

$$\text{Wt. of } Ag \text{ deposited} = Eq.wt\ of\ Ag = 108\ gm$$

$$\text{Wt. of } Ni \text{ deposited} = Eq.wt.\ of\ Ni = 29.5\ gm$$

$$\text{Wt. } of\ Cr \text{ deposited} = Eq.wt.\ of\ Cr = 17.3\ gm$$

.

19. (d) One Faraday $= 1\ gm$ of equivalent of Cu.

20. (c) $W = Zit$; $Z = \frac{E}{96500}$.

21. (d) During electrolysis of $CuSO_4$. Cu^{2+} gets discharged at cathode and OH^- at anode. Thus solution becomes acidic due to excess of H^+ and SO_4^{2-} or H_2SO_4.

23. (b) $1 \text{ mole of electrons} = 1 \text{ faraday}$

$Mg^{++} + 2e^- \rightarrow Mg$;

$2 \text{ moles of electrons} = 2 \text{ faraday}$.

24. (d) $Cu^{++} + 2e^- \rightarrow Cu$

$$E_{Cu} = \frac{63.54}{2} = 31.77$$

Amount of electricity required to deposit .6354 *gm* of *Cu* $= \frac{96500 \times 0.6354}{31.77} = 1930\ Coulombs$.

25. (a) The amount deposited is directly proportional to current intensity, electrochemical equivalent of ions and the time for electrolysis and is independent of the temperature.

27. (a) $W = ZQ$; $W = Zit$.

28. (d) $Ca^{++} + 2e^- \rightarrow Ca$

$$E_{Ca} = \frac{40}{2} = 20$$

$W_{Ca} = E_{Ca} \times$ No. of faradays $= 20 \times 0.04 = 0.8\ gm$.

29. (c) $E_{\text{metal}} = \frac{\text{Weight of metal} \times 96500}{\text{Number of coulombs}}$

$$= \frac{22.2 \times 96500}{2 \times 5 \times 60 \times 60} = 59.5$$

Oxidation number of the metal $= \frac{177}{59.5} = +3$

30. (a) Quantity of electricity passed = $\frac{25}{1000} \times 60 = 1.5$

$2F = 2 \times 96500C$ deposit $Ca = 1 mole$

∴ 1.5 *C* will deposit $Ca = \frac{1}{2 \times 96500} \times 1.5 mole$

$= \frac{1}{2 \times 96500} \times 1.5 \times 6.023 \times 10^{23}$ *atom*

$= 4.68 \times 10^{18}$.

31. (b) Equivalent of *Cl* deposited

= No. of *Faraday* passed = 0.5

Wt. of $Cl = 0.5 \times Eq.wt.$

$= 0.5 \times 35.5 = 17.75\ gm$.

32. (b) At Andoe $At\ Anode\ Cl^- \rightarrow \frac{1}{2} Cl_2 + e^-$

$$E_{Cl_2} = \frac{35.5 \times 2}{2} = 35.5$$

$$W_{Cl_2} = \frac{E_{Cl_2} \times I \times t}{96500}$$

$$= \frac{35.5 \times 2 \times 30 \times 60}{96500} = 1.32\ gm.$$

34. (b) It is Faraday’s law.

35. (b) Equivalent wt. of O_2 = Equivalent wt. of *Cu*

36. (d) $O_2\% = 20\%$

$\text{Metal}\% = 80\% \quad = \frac{80}{20}\times 8 = 32\,g\,\text{of metal}$.

37. (b) $V = \frac{827\times 10^3}{4\times 96500} = 2.14\,V$.

38. (b) $Ag^+ \xrightarrow{+e^-} Ag,$ 96500 *C* will liberate silver =108 *gm*.
9650*C* will liberate silver = 10.8 *gm.*

39. (a) One mole of monovalent metal ion means charge of N electron i.e. 96500 *C* or 1 *Faraday.*

42. (a) 1 Faraday involves charge of 1 *mole* electrons.

43. (a) *Coulomb* = *ampere* (A) × *second* (S).

44. (b) $E = -\frac{13.6}{n^2}$ for He^+ $n = 1$

$E = -\frac{13.6}{1^2} = -13.6\,eV$.

45. (c) $W \propto E$ if *i* and *t* are constant.

47. (d) Charge (Coulombs) pass per second $= 10^{-6}$
number of electrons passed per second

$= \frac{10^{-6}}{1.602\times 10^{-19}} = 6.24\times 10^{12}$.

48. (d) At cathode;

$Fe^{2+} + 2e^- \to Fe$; $Fe^{3+} + 3e^- \to Fe$

$(E_{Fe})_1 = \frac{\text{Atomic weight}}{2}$; $(E_{Fe})_2 = \frac{\text{Atomic weight}}{3}$

Ratio of weight of *Fe* liberated

$= \frac{\text{Atomic weight}}{3} : \frac{\text{Atomic weight}}{2} = 3 : 2$.

49. (b) 31.75 *g* copper gets deposited at cathode on passing 96500 *coulomb* charge. We know that 31.75 *gm* of *Cu* is equal to 0.5 mole of *Cu* deposited at cathode on passing 1*F* of current.

52. (b) For deposition of one equivalent silver required charged is 96500 *C*.

53. (b) $Cu^{++} + 2e^- \to Cu$;

$E_{Cu} = \frac{63.55}{2} = 31.75\,gm\,Cu$.

54. (a) $Q = 2.5\times 386 = 96500C$

$2F(2\times 96500C)$ deposited $Cu = 63.5\,g$

∴Hence 965 *C* will deposited; $Cu = 0.3175\,gm$.

55. (c) $\frac{\text{Wt. of } Cu}{\text{Wt. of } Ag} = \frac{\text{Eq. wt. of } Cu}{\text{Eq. wt. of } Ag}$;

$\frac{\text{Wt. of } Cu}{1.08} = \frac{63.5/2}{108}$

Wt. of $Cu = 0.3177\,gm$.

56. (c) 1 *g* atom of *Al* = 3 equivalent of $Al = 3$ faraday charge
3 *mole* electrons = 3 *N* electron.

57. (c) At cathode : $Al^{3+} + 3e^- \to Al$

$E_{Al} = \frac{\text{Atomic mass}}{3}$

At cathode : $Cu^{2+} + 2e^- \to Cu$

$E_{Cu} = \frac{\text{Atomic mass}}{2}$

At cathode : $Na^+ + e^- \to Na$

$E_{Na} = \frac{\text{Atomic mass}}{1}$

For the passage of 3 faraday;
mole atoms of Al deposited = 1
mole atoms of *Cu* deposited $= \frac{1\times 3}{2} = 1.5$
mole atoms of *Na* deposited $= 1\times 3 = 3$.

58. (d) At cathode: $Ag^+ + e^- \to Ag$

At Anode: $2OH^- \to H_2O + \frac{1}{2}O_2 + 2e^-$

$E_{Ag} = \frac{108}{1} = 108$; $E_{O_2} = \frac{\frac{1}{2}\times 32}{2} = 8$

$\frac{W_{Ag}}{E_{Ag}} = \frac{W_{O_2}}{E_{O_2}}$; $W_{Ag} = \frac{1.6\times 108}{8} = 21.6\,gm$.

59. (d) *KI* is an electrolyte.

60. (d) Number of *gm* equivalent = Number of faraday pass

4 *gm* = 4 faraday.

61. (c) Eq. of *Al* = $\frac{13.5}{27/3} = 1.5$.

Thus 1.5 Faraday is needed.

63. (b) Electricity required
= No. of *gm* equivalent × 96500 *coulombs*
= 0.5 × 96500 = 48250 *C.*

64. (a) Equivalent weight of silver = 107.870 *g*.
1 Faraday = 96500 *coulomb.*

67. (a) Equivalent weight and atomic weight of *Na* metal are the same, so 1*g* atom of *Na* is deposited by one Faraday of current.

68. (a) $Al \to Al^{3+} + 3e^-$.

70. (c) ∵ 1*F* obtained from 1 *g* equivalent
∴ 2.5 *F* obtained from 2.5 *g* equivalent.

75. (c) Faraday constant depends upon the current passed.

80. (b) In 5 *gm CuO*, 4 *gm Cu* and 1 *gm O* be present.

Element	Wt.	At Wt.	$Wt./At.Wt. \neq$	Ratio
Cu	4 *gm*	63.5	4/63.5=.0625	$\frac{.0625}{.0625} = 1$

O	1 gm	16	1/16 =.0625	$\frac{.0625}{.0625} = 1$

Emperical formula = CuO of oxide

In this oxide, oxidation no. of $Cu = +2$

Equivalent weight

$= \frac{\text{Molecularweight}}{\text{Oxidationno.}} = \frac{63.5}{2} \approx 31.75$ but

Equivalent weight should be an integeral no. = 32

81. (c) Given, Current = 241.25 *columb*

1 *coulomb* current will deposite

$= 1.118 \times 10^{-3}\, gm\, Ag$.

∴ 241.25 current will deposite =

$1.118 \times 10^{-3} \times 241.25$

$= 0.27\, gm$ silver.

82. (b) Reaction for electrolysis of water is

$2H_2O \rightleftharpoons 4H^+ + 2O^{2-}$

$2O^{2-} \to O_2 + 4e^-$

$4e^- + 4H^+ \to 2H_2$

∵ $n = 4$ so 4 Faraday charge will liberate

1 mole $= 22.4\, dm^3$ oxygen

∴ 1 Faraday charge will liberate

$\frac{22.4}{4} = 5.6\, dm^3\ O_2$.

83. (a) $Na^+ + e^- \to Na$

Charge (in *F*) = moles of e^- used = moles of *Na* deposited

$= \frac{11.5}{23}\, gm = 0.5$ *Faraday.*

84. (c) Hydrolysis of water : $2H_2O \rightleftharpoons 4H^+ + 4e^- + O_2$

4 *F* charge will produce = 1 mole $O_2 = 32\, gm\, O_2$

1 *F* charge will produce $= \frac{32}{4} = 8\, gm\, O_2$.

85. (c) In a galvanic cell, the electrons flow from anode to cathode through the external circuit. At anode (–*ve* pole) oxidation and at cathode (+ pole) reduction takes place.

86. (e) Number of equivalents of silver formed = Number of equivalents of copper formed.

In $AgNO_3$, Ag is in +1 oxidation state.

In $CuSO_4$, Cu is in +2 oxidation state.

Equivalent weight of *Ag* = $\frac{108}{1} = 108$

Equivalent weight of *Cu* $= \frac{63.6}{2} = 31.8$

$\frac{M_1}{M_2} = \frac{E_1}{E_2}$; $\frac{10.79}{M_{Cu}} = \frac{108}{31.8}$

$M_{Cu} = \frac{10.79 \times 31.8}{108} = 3.2\, gm.$

87. (b) Laws of electrolysis were proposed by Faraday.

88. (a) Given, Current (*i*) = 25 mA = 0.025 A

Time (*t*) = 60 *sec*

Q = *i t* $= 60 \times 0.025 = 1.5$ *coulombs*

No. of electrons $= \frac{1.5 \times 6.023 \times 10^{23}}{96500}$

$e^- = 9.36 \times 10^{18}$

$Ca \to Ca^{2+} + 2e^-$

$2e^-$ are required to deposite one *Ca* atom

$9.36 \times 10^{18}\ e^-$ will be used to deposite

$= \frac{9.36 \times 10^{18}}{2} = 4.68 \times 10^{18}$.

89. (d) $C_6H_5NO_2 + 6H^+ + 6e^- \to$

$C_6H_5NH_2 + 2H_2O$

1 mole = 123 *gm* nitrogen requires 6 mole electron *e*

$= 6 \times 96500\, coulomb$ *charge*

∴ 12.3 *gm* nitrobenzene will require

$= \frac{6 \times 96500 \times 12.3}{123} = 6 \times 9650 = 57900\, C.$

90. (c) *Au* and *Ag* settle down below the anode as anode mud during the process of electrolytic refining of copper.

Conductor and Conductance

2. (b) $\lambda^\infty BaCl_2 = \frac{1}{2}\lambda^\infty Ba^{2+} + \lambda^\infty Cl^-$

$= \frac{127}{2} + 76 = 139.5\ ohm^{-1}\ cm^{-1}\ eq^{-1}$.

3. (d) Dilution, temperature and nature of electrolyte affect the conductivity of solution.

5. (a) Generally strong electrolyte on dilution shows conductivity characters.

6. (b) Molar conductivity = $\frac{1000}{MX}$.

7. (b) $C = \frac{K[A]A}{l}$, $K = \frac{C \times l}{[A]A}$

$= \frac{Sm}{mol\, m^{-3}\, m^2} = Sm^2 mol^{-1}$.

9. (b) Conductivity of a solution is directly proportional to the number of ions.

11. (a) $NaCl \rightleftharpoons Na^+ + Cl^-$. So it conduct electricity.

12. (b) Graphite is a good conductor of electricity.

15. (b) Electrolytic conduction resistance decreases with increasing temperature.

16. (d) Because conductance is increase when the dissociation is more.

17. (b) Strong electrolyte ionize completely at all dilutions and the number of ions does not increase on dilution. A small increase in $\wedge_m$ volume with dilution is due to the weakening of electrostatic attraction between the ions on dilution.

18. (d) In electrolytic conductors, a single stream of electrons flow from cathode to anode.

19. (b) In solid state $NaCl$ does not dissociate into ions so it does not conduct electricity.

20. (c) The ions are not free to move in solid state and held up in lattice due to strong coulombic forces of attraction.

21. (b) C_2H_5OH being non electrolyte so does not ionize.

22. (a) Since molar conductance $\propto \frac{1}{\text{Molarity}}$.

23. (c) Molar condcutivity $= \frac{1}{\rho M}$

So its unit will be $\Omega^{-1} cm^2 mol^{-1}$.

25. (a) $l/a = 0.5\, cm^{-1}, R = 50\, ohm$

$$p = \frac{Ra}{l} = \frac{50}{0.5} = 100$$

$$\Lambda = k \times \frac{1000}{N} = \frac{1}{p} \times \frac{1000}{N} = \frac{1}{100} \times \frac{1000}{1}$$

$10\, ohm^{-1} cm^2\, gmeq^{-1}$

26. (b) $\Lambda^o_{m(C_6H_5COOH)} = \Lambda^o_{(C_6H_5COO^-)} + \Lambda^o_{(H^+)}$

$= 42 + 288.42 = 330.42$

$$\alpha = \frac{\Lambda^c_m}{\Lambda^o_m} = \frac{12.8}{330.42} = 3.9\%$$

27. (d) Conductance $= \frac{1}{\text{resistance}} = \frac{1}{ohm} = ohm^{-1}$

or mho

Cell constant and Electrochemical cells

1. (d) In the absence of electric field the ions in the solution move randomly due to thermal energy.

2. (d) Since E^o_{A/A^-} has large negative value, the tendency of *A* to be reduced to A^- is very small. In other words tendency of A^- to be oxidized to *A* is very large.

3. (d) Practically only 60-70% efficiency has been attained.

4. (b) $K = \frac{1}{R} \times$ Cell constant

Cell constant $= K \times R$; $0.012 \times 55 = 0.66\, cm^{-1}$.

5. (b) In common dry cell.

Anode : $Zn \to Zn^{++} + 2e^-$

Cathode: $2MnO_2 + Zn^{++} + 2e^- \to ZnMn_2O_4$.

6. (a) Because the reduction potential of Cu is highest.

7. (c) Overall reaction - $2H_{2(g)} + O_{2(g)} \to 2H_2O(l)$.

9. (b) During charging of a lead storage battery, the reaction at the anode and cathode are

Anode: $PbSO_4 + 2e^- \to Pb + SO_4^{2-}$

Cathode:

$PbSO_4 + 2H_2O \to PbO_2 + 4H^+ + SO_4^{2-} + 2e^-$

In both the reactions H_2SO_4 is regenerated.

11. (c) $2NH_4Cl + Zn \to 2NH_3 + ZnCl_2 + H_2 \uparrow$.

13. (a) When platinum electrodes are dipped in dilute solution H_2SO_4 than H_2 is evolved at cathode.

14. (a) Electrode on which oxidation occurs is written on $L.H.S.$ and the other on the $R.H.S.$ as represented by

$Zn | Zn^{2+} || Cu^{2+} | Cu$.

15. (d) $\overbrace{Zn^{2+} + 2e^- \to Zn}^{\text{Reduction}}$. It shows reduction reaction.

16. (c) In the electrolytic cell electrical energy change into chemical energy.

17. (c) In the cell $Zn | Zn^{2+} || Cu^{2+} | Cu$ the negative electrode (anode) is *Zn*. In electrochemical cell representation anode is always written on left side while cathode on right side.

18. (a) Galvanic cell converts the chemical energy into electrical energy.

19. (b) Fuel-cells are used to provide power and drinking water to astronauts in space programme.

21. (b)

$$E^o_{cell} = \frac{2.303\, RT}{nF} \log K = \frac{0.0591}{n} \log K_c \text{ at } 298K$$

.

22. (b) $\underbrace{Cu^{2+} + 2e^- \to Cu}_{\text{Reduction}}$

24. (b) The cell in which *Cu* and *Zn* roads are dipped in its solutions called Daniel cell.

25. (c) $K = C \times \text{Cell constant} = \frac{K}{C} = \frac{0.2}{0.04} = 5\, cm^{-1}$.

26. (a) $\frac{K}{C} =$ Cell Constant.

27. (c) Velocities of both K^+ and NO_3^- are nearly the same in KNO_3 so it is used to make salt-bridge.

28. (a) In this reaction 4 electrons are needed for the reaction volume.

29. (b) In electrochemical cell H_2 release at anode and *Cu* is deposit at the cathode.

31. (a) Anode has negative polarity.

32. (b) $\wedge_m^o (CH_3COOH) =$

$\wedge^o (CH_3COONa) + \wedge^o (HCl) - \wedge^o (NaCl)$

$= 91 + 426.16 - 126.45 = 390.71\ ohm^{-1} cm^2 mol^{-}$

.

36. (b) At anode: $Zn_{(s)} \rightarrow Zn^{2+} + 2e^-$.

38. (d) $PbSO_4 + 2H_2O \rightarrow 2PbO_2 + 4SO_4^{--} + 2e^-$.

39. (b) MnO_2 is used in dry batteries cell.

40. (d) $Pb + PbO_2 + 2H_2SO_4 \underset{\text{Recharge}}{\overset{\text{Discharge}}{\rightleftharpoons}}$
$2PbSO_4 + 2H_2O$.

Sulphuric acid is consumed on discharging.

42. (d) The metal placed below in electrochemical series does not react with that metal salt solution which metal is placed above in series.

43. (c) In the electrochemical cell chemical energy changes into electrical energy.

44. (a) In galvanic cell, the salt bridge used to complete the circuit.

45. (d) $Cu + FeSO_4 \rightarrow \text{No reaction}$ Because *Cu* has $E^o = 0.34$ *volt* and Fe has $E^o = -0.44$ *volt*.

47. (d) Calomel electrode as reference electrode is made by using Hg_2Cl_2.

48. (b) In hydrogen–oxygen fuel cell following reactions take place to create potential difference between two electrodes.

$$2H_{2(g)} + 4OH^-_{(aq)} \rightarrow 4H_2O_{(l)} + 4e^-$$

$$O_{2(g)} + 2H_2O_{(l)} + 4e^- \rightarrow 4OH^-_{(aq)}$$

Overall reaction = $2H_{2(g)} + O_{2(g)} \rightarrow 2H_2O_{(l)}$

the net reaction is the same as burning (Combustion) of hydrogen to form water.

49. (c)

$$\underset{\lambda_{ClCH_2COONa}}{ClCH_2COONa} + \underset{\lambda_{HCl}}{HCl} \rightarrow \underset{\lambda_{ClCH_2COOH}}{ClCH_2COOH} + \underset{\lambda_{NaCl}}{NaCl}$$

$$\lambda_{ClCH_2COONa} + \lambda_{HCl} = \lambda_{ClCH_2COOH} + \lambda_{NaCl}$$

$224 + 203 = \lambda_{ClCH_2COOH} + 38.2$

$\lambda_{ClCH_2COOH} = 427 - 38.2 = 388.8\ ohm^{-1} cm^2 gmeq^{-}$

.

50. (c) In daniel cell copper rod acts as cathode so there cations move towards copper electrode and reduction take place on copper rod.

51. (b) Elements with lower reduction potential act as anode. His placed above *Cu* in electrochemical series so it has lesser reduction potential and thus act as anode and *Cu* act as cathode.

52. (d) Fuel cells are more efficient as they are free from pollution and hence they run till the reactants are active. They have longer life than lead storage cells.

53. (c) For gold plating, the used electrolyte is $K[Au(CN)_2]$.

54. (a) Dil. H_2SO_4 is used in lead in lead storage battery as electrolyte.

55. (c) Cell constant $= \dfrac{\text{Specificconductivity}}{\text{Observedconductance}}$

$= \dfrac{0.002765}{1/R}$ =$0.002765 \times 400 = 1.106$.

57. (b) $2AgCl_{(s)} + H_{2(g)} \rightarrow 2HCl_{(aq.)} + 2Ag_{(s)}$

The activities of solids and liquids are takes as unity and at low concentrations, the activity of a solute is approximated to its molarity.

Th cell reaction will be

$Pt_{(s)} \mid H_{2(g)}$, 1 bar $\mid H^+_{(aq)}$ 1 $M \mid AgCl_{(aq)}$ 1 $M \mid Ag_{(s)}$

58. (a) $E_{cell} = \dfrac{0.059}{n} \log \dfrac{1}{C} = -\dfrac{0.059}{2} \log \dfrac{1}{100}$

$= -\dfrac{0.059}{2}(-2) = 0.059V = 59mV$.

(increase)

59. (a) $E_{cell} = -0.059 \log \dfrac{10^{-6}}{10^{-3}} = -0.059 \log 10^{-3}$

$= -0.059 \times (-3) = 0.177V$.

60. (c) The magnitude of the electrode potential of a metal is a measure of its relative tendency to lose or gain electrons. *i.e.,* it is a measure of the relative tendency to undergo oxidation (loss of electrons) or reduction (gain of electrons).

$M \rightarrow M^{n+} + ne^-$ (oxidation potential)

$M^{n+} + ne^- \rightarrow M$ (reduction potential)

61. (a) On electrolysis of fused ionic hydride (LiH), hydrogen obtained at anode.

$MH + H_2O \rightarrow MOH + H_2\uparrow$

Electrode potential, E_{cell}, Nernst equation and ECS

1. (b) Reduction potential of hydrogen electrode,

$E_H = \dfrac{-2.303RT}{F} \log \dfrac{1}{[H^+]}$

$= -0.059\,pH = -0.059 \times 3 = -0.177V$.

2. (a) $E^o_{\text{cell}} = E^o_{\text{cathode}} - E^o_{\text{anode}} =$
$0.799 - (-0.763) = 1.562\,V$

3. (a) More negative is the reduction potential, higher will be the reducing property, *i.e.* the power to give up electrons.

4. (b) Standard potential of Zinc < Copper.

6. (c) A cation having highest reduction potential will be reduced first and so on. However, Mg^{2+} in aqueous solution will not be reduced $\left(E^0_{Mg^{2+}/Mg} < E_{H_2O/\frac{1}{2}H_2+OH^-}\right)$. Instead water would be reduced in preference.

7. (c) A is displace from *D* because *D* have a $E^o = -0.402\,V$

Reductio
n

8. (a) $\overset{0}{Zn}_{(s)} + 2Ag^+_{(aq)} \rightarrow Zn^{2+}_{(aq)} + 2\overset{0}{Ag}_{(s)}$

Oxidation

In this reaction zinc act as a anode and Ag act as a cathode.

9. (a) No doubt Be is placed above Mg in the second group of periodic table but it is below Mg in electrochemical series.

10. (b) Nernst's equation shows relation between E and E^o.

11. (a) $E = E^o - \frac{RT}{nF}\ln\frac{1}{[M^{n+}]}$; $E = E^o + \frac{RT}{nF}\ln[M^{n+}]$

$$E = E^o + \frac{2.303RT}{nF}\log[M^{n+}]$$

Substituting the value of *R*, *T* (298*K*) and *F* we get

$$E = E^o + \frac{0.0591}{n}\log(M^{n+}).$$

12. (c) At 298 *K* standard electrode potential of NHE electrode is 0.00 *V.*

13. (a) Since, Ag^+ ions are reduced to *Ag* and $E^o_{Ag^+/Ag} > E^o_{Cu^{++}/Cu}$ *Cu* is oxidized to Cu^{++}.

14. (d) The reducing power decreases as the reduction potential increase (becomes less negative).

15. (c) Actually the equation is derived from Nerst equation assuming equilibrium condition in a cell reaction, when $E = 0$.

16. (a) More negative is the standard reduction potential, greater is the tendency to lose electrons and hence greater reactivity.

17. (a) Hg has greater reduction potential than that of H^+ and hence cannot displace hydrogen from acid.

18. (c) Brown layer is deposited on iron rod because Cu has greater reduction potential than that of Fe^{2+}.

19. (b) Since $E^o_{A^{2+}/A} < E^o_{B^{2+}/B}$. A has greater tendency to be oxidized.
$A + B^{2+} \rightarrow A^{2+} + B$.

20. (b) Since $E^o_{Zn^{++}/Zn}$ is negative, so *Zn* has greater tendency to be oxidized than hydrogen. Hence it can act as reducing agent.

21. (a) Standard electrode potential of Hydrogen is zero.

22. (b) According to electrochemical series.

23. (a) The standard reduction potential of K^+, Mg^{2+}, Zn^{+2} Cu^{2+} increase in this order.

24. (c) $E_{\text{cell}} = E^o_{Au^{3+}/Au} - E^o_{Ni^{2+}/Ni}$
$= 1.50 - (-0.25) = 1.75\,V.$

25. (a) Electromotive force is *+ve* if oxidation and reduction both takes place in a cell.

28. (a) In galvanic cell anode always made up of negative electrode.

29. (d) $\overset{\text{Anode}}{A \mid A^+(a=1)} \,||\, \overset{\text{Cathode}}{B^+(a=1) \mid B}$
$EMF = E_{cathode} - E_{anode} = 0.75 - (0.5)$;
$EMF = 0.25\,V$.

30. (d) $E^o = -3.05\,Li^+/Li$ is most negative (minimum) and hence Li has maximum tendency to lose electrons or it is the strongest reducing agent.

31. (b) Brown layer is deposited on iron rod because *Cu* has greater than reduction potential than that of Fe^{2+}.

32. (a) $E^o_{Zn^{++}/Zn} < E^o_{Fe^{++}/Fe}$, so *Zn* will reduce Fe^{++}. Zn cannot reduce Mg^{2+} because $E^o_{Zn^{++}/Zn} > E^o_{Mg^{++}/Mg}$
On similar reason *Mg* and Zn cannot oxidize Fe.

33. (d) For the cell reaction, *Fe* acts as cathode and *Sn* as anode. Hence,
$E^o_{cell} = E^o_{\text{cathode}} - E^o_{\text{anode}}$ = – 0.44 – (– 0.14)= – 0.30*V*
The negative *EMF* suggests that the reaction goes spontaneously in reversed direction.

34. (a) $E^o_{\text{cell}} = E^o_{\text{cathode}} - E^o_{\text{anode}} = 0.34 - (-0.76)$
$= 1.10\,V$.

35. (c) $E^o_{\text{cell}} = E^o_{\text{cathode}} - E_{\text{anode}}$;
$E^o_{\text{cell}} = 0.34 - (-2.37)$
$E^o_{\text{cell}} = 2.71\,V$.

36. (d) *Mg* lies above *Cu* in electrochemical series and hence *Cu* electrode acts as cathode

$E^o_{cell} = E^o_{Cu^{++}/Cu} - E^o_{Mg^{++}/Mg}$

$2.70\ V = 0.34 - E^o_{Mg^{++}/Mg}$;

$E^o_{Mg^{++}/Mg} = -2.36\ V$.

37. (a) Because H_2 has greater reduction potential so it reduced the Ag^+.

39. (d) $\Delta G^o = -nE^oF$

$Fe^{2+} + 2e^- \rightarrow Fe$ .....(i)

$\Delta G^o = -2 \times F \times (-0.440\,V) = 0.880F$

$Fe^{3+} + 3e^- \rightarrow Fe$ .....(ii)

$\Delta G^o = -3 \times F \times (-0.036) = 0.108F$

On subtracting equation (i) from (ii)

$Fe^{3+} + e^- \rightarrow Fe^{2+}$

$\Delta G^o = 0.108F - 0.880F = -0.772F$

E^o for the reaction $= -\dfrac{\Delta G^o}{nF}$

$= -\dfrac{(-0.772F)}{1 \times F} = +0.772V$.

40. (d) Reducing power *i.e.* the tendency to lose electrons increases as the reduction potential decreases.

41. (b) Cu^{++} will be reduced and Fe will be oxidized.

$Cu^{++} + Fe \rightarrow Cu + Fe^{++}$.

42. (c) Cell reaction is

$Cu_{(s)} + 2Ag^+ \rightarrow Cu^{2+} + 2Ag$

Two half cell reaction is

$Cu \rightarrow Cu^{2+} + 2e^-$ Oxidation (anode)

$Ag^+ + e^- \rightarrow Ag$ Reduction (cathode)

$E_{Cell} = E_{ox} - E_{Red} = 0.80 - 0.34 = +0.46V$

43. (a) EMF = [s.r.p. of cathode–s.r.p of anode]

Where s.r.p. = Standard reduction potential

If EMF is positive then the reaction is spontaneous

For *e.g.* in Galvanic cell

(a) EMF = 1.1 *volt*

(b) Cathode is made of copper

(c) Anode is made of Zinc

EMF = 0.34 –(– 0.76) = 1.1 *volt.*

46. (d) H_2 is anode because oxidation takes place.

Cu is cathode because reduction is takes place.

47. (c) $E^o_{cell} = E_{cathode} - E_{anode}$.

51. (b) Standard hydrogen electrode have zero electrode potential.

53. (a) $\Delta G = -nFE^o$

$\Delta G = -1 \times 96500 \times 1.02$; $\Delta G = -98430$.

54. (c) Fuel cell converts the chemical energy into electrical energy.

55. (a) $E = E^o - \dfrac{2.303\,RT}{nF}\log\dfrac{[M]}{[M^{n+}]}$.

56. (a) Less is the reduction potential stronger is the reducing agent.

57. (a) Reducing power, *i.e.* the tendency to lose electrons increases as the reduction potential decreases.

58. (a) $OCl^- \rightarrow C^-, E^o = 0.94V$

$Cl^- \rightarrow \dfrac{1}{2}Cl_2 + e^- E^o = -1.36V$

adding the two equations, we get

$OCl^- \rightarrow \dfrac{1}{2}Cl_2, E^o = 0.94 - 1.36 = -0.42V$.

60. (a) It cannot evolved H_2 from H_2S

$Hg + H_2S \rightarrow$ No reaction.

61. (b) $E^o_{cell} = \dfrac{0.059}{n}\log K$

$\log K = \dfrac{1.10 \times 2}{0.059} = 37.2881$ or $K = 10^{-37}$.

62. (d) The oxidizing character *i.e.* acceptance of electrons increases with the reduction potential.

63. (a) According to electrochemical series.

64. (d) $E_{cell} = E^o_{cell} - \dfrac{RT}{nF}\ln\dfrac{C_2}{C_1}$ and $\Delta G = -nF\,E_{cell}$

hence ΔG is the function of $\ln\left(\dfrac{C_2}{C_1}\right)$.

66. (c) $E = E^o - \dfrac{0.059}{n}\log\dfrac{[Zn^{++}]}{[Cu^{++}]}$

$= 1.10 - \dfrac{0.059}{2}\log\dfrac{1}{0.1}$

$= 1.10 - 0.0295\log 10 = 1.07\,volt$.

67. (b)

$E_1 = E_o - \dfrac{0.0591}{2}\log\dfrac{0.01}{1} = E_o + \dfrac{0.0591}{2} \times 2$

$E_2 = E_o - \dfrac{0.0591}{2}\log\dfrac{100}{0.01} = E_o - \dfrac{0.0591}{2} \times 4$

$\therefore E_1 > E_2$.

68. (b) $\underbrace{Fe^{+2} + \overbrace{Zn \rightarrow Zn^{2+}}^{\text{Oxidation}} + Fe}_{\text{Reduction}}$

$EMF = E_{cathode} - E_{anode}$

$= 0.44 - (0.76) = +0.32V$.

69. (a) *Fe* is more electropositive than copper. Hence Cu^{2+} can oxidise *Fe*.

70. (b) $E^o = 0$ because hydrogen have zero potential.

71. (b) Cell potential of the cell is positive.

72. (a,b) Because these comes after the *Fe* in electrochemical series.

73. (c)

Oxidation

$Fe^{2+} + Zn \rightarrow Zn^{2+} + Fe$

Reduction

$EMF = E_{\text{cathode}} - E_{\text{anode}}$

$= -7.81 - (-7.62)$

$EMF = -0.19V$.

74. (c) $Cr^{3+} > Zn^{2+} > H > Fe^{3+}$.

Reducing nature decreasing order.

75. (a) More is reduction potential, more is the power to get itself reduced or lesser is reducing power or greater is oxidising power.

76. (d) $\Delta G = -nFE^o$

$\Delta G = -2.303RT \log K$;

$nFE^o = 2.303RT \log K$

$$\log K = \frac{nFE^o}{2.303RT} = \frac{2 \times 96500 \times 0.295}{2.303 \times 8.314 \times 298}$$

$\log K = 9.97 = K = 1 \times 10^{10}$.

77. (b) For the given cell $M | M^+ || X^- | X$, the cell reaction is derived as follows:

RHS: reduction $X + e^- \rightarrow X^-$ .....(i)

LHS: Oxidation $M \rightarrow M^+ + e^-$ .....(ii)

Add (i) and (ii) $M + X \rightarrow M^+ + X^-$

The cell potential = $-0.11V$

Since E_{cell} = – ve, the cell reaction derived above is not spontaneous. In fact, the reverse reaction will occur spontaneously.

78. (c) $\overset{0}{Zn} + \overset{+2}{Mg}Cl_2 \rightarrow \overset{+2}{Zn}Cl_2 + Mg$ No reaction

Oxidation

Reduction

This type of reaction does not occur because $Mg^{2+} E^o = -2.37V$ while $Zn^{2+} E^o = -0.76V$.

79. (b) In neutral medium Mn^{+7} oxidation state change into +4 oxidation state, hence equivalent weight of $KMnO_4 = \frac{M}{3}$.

80. (a) Increase in the concentration of Ag^+ ion increase the voltage of the cell.

81. (a) $E_{\text{cell}} = E^o_{\text{cell}} + \frac{0.059}{2} \log \frac{(Ag^+)}{(Sn^{2+})}$.

82. (b) The *K.E.* of proton is 1 *KeV.*

83. (b) Anodic reaction : $H_2(P_1) \rightarrow 2H^+$

Cathodic reaction : $2H^+ \rightarrow H_2(P_2)$

$$E_{cathode} = -\frac{RT}{2F} \ln \frac{P_2}{[H^+]^2};$$

$$E_{\text{anode}} = -\frac{RT}{2F} \ln \frac{[H^+]^2}{P_1}$$

$$E_{\text{inf}} = E_{anode} + E_{cathode}$$

$$= -\frac{RT}{2F} \ln \frac{(H^+)^2}{P_1} - \frac{RT}{2F} \ln \frac{P_2}{(H^+)^2}$$

$$= -\frac{RT}{2F} \ln \frac{P_2}{P_1} = \frac{RT}{2F} \ln \frac{P_1}{P_2}.$$

84. (c) $\frac{1}{2} H_2 \rightarrow H^+(10^{-8} M) + e^-$(oxidation)

$H^+(0.025M) + e^- \rightarrow \frac{1}{2} H_2$(reduction)

Cell reaction is :

$H^+(0.025M) \rightarrow H^+(10^{-8} M)$;

$E_{\text{cell}} = 0.38\ V$.

85. (a) E^o *for Fe / Fe*$^{2+}$ $= 0.44$ V .

86. (c) (Reduction potential of cathode) – (reduction potential of anode).

87. (a) The correct decreasing electrode potential order is : K, Ba, Ca, Mg.

89. (c) $E^o_{cell} = E^o_{cathode} - E^o_{anode}$

$= 0.34 - (-2.37) = +2.71\ V$.

90. (b) Because flourine is most powerful reducing agent than other halogens.

92. (c) Aluminium forms a protective oxide layer but iron does not.

93. (d) The reduction potential of *Zn* is very higher than *Cu*.

94. (a) The *pH* of 0.1 *M* HCl and 0.1 *M* acetic acid is not the same, because HCl is a strong acid so its *pH* is less and CH_3COOH is a weak acid, so its *pH* is more.

95. (d) The required reaction $(Cu^{++} + Cu \rightarrow 2Cu^+)$ can be obtained by using the following reactions.

$Cu^{++} + e^- \rightarrow Cu^+$; $E^o_{Cu^{++}/Cu^+} = 0.15\ V$

.....(i)

$Cu^{++} + 2e^- \rightarrow Cu$; $E^o_{Cu^{++}/Cu} = 0.34\ V$

.....(ii)

Multiplying eq. (i) by 2 we get

$2Cu^{++} + 2e^- \rightarrow 2Cu^+$ .....(iii)

$\Delta G_1 = -nFE = -2 \times F \times 0.15$

$Cu^{++} + 2e^- \rightarrow Cu$ .....(iv)

$\Delta G_2 = -nFE = -2 \times F \times 0.34$

Subtract the *eq*. (iv) from (iii)

$Cu^{++} + Cu \rightarrow 2Cu^+$

$\Delta G_3 = -nFE = -1 \times F \times E^o$

Also $\Delta G_3 = \Delta G_1 - \Delta G_2$

$-1FE^o = (-2F \times 0.15) - (-2F \times 0.34)$

$E^o = -0.38$

This is the value for the reaction

$Cu^{++} + Cu \rightarrow 2Cu^+$

But the given reaction is just reverse of it

$\therefore E_{\text{cell}}$ for given reaction = + 0.38*V*.

97. (d) It connect two solutions and complete the circuit.

98. (a) Greater the oxidation potential, greater is the reactivity.

99. (b) Electrochemical series compare the relative reactivity of metals.

100. (d) Fuel cells are more efficient, free from pollution and they run till reactants are active.

102. (c) $E^o = E^o_{Ag^{2+}/Ag} + E^o_{Cu/Cu^{2+}}$

$= -0.34 + 0.80 = +0.46\,V$.

103. (a) *Fe* is placed above *Cu* in electrochemical series.

104. (a) Lithium is the strongest reducing agent of the alkali metals.

105. (d) Potassium is more electropositive element, because it is the only alkali metal among the given elements.

106. (b) Aluminium forms a self protecting film of oxide to prevent corrosion.

107. (a) $Zn_{(s)} + 2H^+(aq) \rightleftharpoons Zn^{2+}_{(aq)} + H_{2(g)}$

$$E_{Cell} = E^0_{Cell} - \frac{.059}{2}\log\frac{[Zn^{2+}]}{[H^+]^2}$$

When H_2SO_4 is added then $[H^+]$ will increase therefore E_{Cell} will also increases and equilibrium will shift towards right.

108. (b) For $M^+ + X^- \rightarrow M + X$

$E^0_{Cell} = E^0_{Cathode} + E^0_{Anode}$

$= 0.44 - 0.33 = +0.11\,V$

Since $E^0_{Cell} = (+)\,0.11\,V$ is positive hence this reaction should be spontaneous.

109. (a) $E_{Cell} = E^0_{Cell} - \dfrac{0.0591}{n}\log K_c$

At 298 *K* $E_{Cell} = 0$ $O = 0.591 - \dfrac{0.0591}{n}\log K_c$

$\log K_c = \dfrac{0.591 \times 1}{0.0591} = 10$;

$K_c = \text{Antilog}10 = 1 \times 10^{10}$.

110. (a) $\frac{1}{2}H_2 \,|\, H^+ \,|\,\,|\, Ag^+ \,|\, Ag \,|$

$E^0_{Cell} = E^0_{Cathode} - E^0_{Anode} = E^0_{Ag^+/Ag} - E^0_{H^+/\frac{1}{2}H_2}$

$(0.80) - (0.0) = 0.80\,V$.

111. (a) $E_A = 2.23V > E_B = 1.43\,V$

So *A* will act as cathode in galvanic cell. Hence

$E^0_{Cell} = E_{Cathode} - E_{Anode} = E_A - E_B$

$= (2.23) - (-1.43) = 3.66\,V$.

112. (b) $E^0_{Cu} > E^0_{Mg}$ hence *Cu* acts as cathode and *Mg* acts as anode.

$E^0_{Cell} = E^0_{Cu} - E^0_{Mg}$

$= (0.34) - (-2.37) = +2.71\,V$.

113. (b) In this cell *Co* is oxidised and it acts as anode and *Ce* acts as cathode.

$E^0_{Cell} = E^0_{Cathode} - E^0_{Anode}$

$= 1.89 = E^0_{Cell} - (-0.28)$

$E^0_{Cell} = 1.89 - 0.28 = 1.61$ *Volts*.

114. (b) Given: $\Delta G = -21.20\,kJ = 21200J$

$\because \Delta G = -nFE$

$$E = \frac{21200}{1 \times 96500} = 0.2196\,V = 0.22\,V.$$

115. (b) $Ag \,|\, Ag^+(.1m) \,|\,|\, Ag^+ 1M \,|\, Ag \,|$

$$E_{Cell} = \frac{2.303RT}{nF}\log\frac{c_1}{c_2} = \frac{0.059}{1}\log\frac{1}{0.1}$$

$= 0.059\log 10 = 0.059$ *Volt*.

116. (b) For this cell, reaction is: $Zn + Fe^{2+} \rightarrow Zn^{2+} + Fe$

$$E = E^0 - \frac{0.0591}{n}\log\frac{c_1}{c_2};$$

$$E^0 = E + \frac{0.0591}{n}\log\frac{c_1}{c_2}$$

$$= 0.2905 + \frac{0.0591}{2}\log\frac{10^{-2}}{10^{-3}} = 0.32\,V.$$

$$E^0 = \frac{0.0591}{2}\log K_c;$$

$$\log K_c = \frac{0.32 \times 2}{0.0591} = \frac{0.32}{0.0295}$$

$$\therefore K_c = \frac{0.32}{10^{0295}}.$$

117. (d) *Al* displaces *H* from *HCl* but silver cannot it means *Al* is situated above the *Ag* in *ECS*, hence *Al* will acts as anode and *Ag* will act as cathode.

$E^0_{Cell} = E^0_{Cathode} - E^0_{Anode} = E^0_{Ag^+/Ag} - E^0_{Al^{3+}/Al}$

$2.46 = 0.8 - E^0_{Al^{3+}/Al}$;

$E^0_{Al} = 0.8 - 2.46 = -1.66\,V$.

118. (a) For $Sn_{(s)} + 2Fe^{3+}_{(aq)} \rightarrow 2Fe^{2+}_{(aq)} + Sn^{2+}_{(aq)}$

$$E^0_{Cell} = E^0_{Sn/Sn^{2+}} + E^0_{Fe^{3+}/Fe^{2+}} = (0.14) + (0.77)$$

$E_{Cell} = 0.91\ Volts$.

119. (d) I^- get oxidised to I_2 hence will form anode and $Cr_2O_7^{2-}$ get reduced to Cr^{3+} hence will form cathode.

$E^0_{Cell} = E^0_{Cathode} - E^0_{Anode}$; $E^0_{Cell} = E_{Cr_2O_7^{-2}} - E^0_{I_2}$

$0.79 = 1.33 - E^0_{I_2}$; $E^0_{I_2} = 1.33 - 0.79$;

$E^0_{I_2} = 0.54\ V$.

120. (b) According to nernst's equation

$$E_{Cell} = E^0_{Cell} - \frac{nRT}{F}\log\frac{c_1}{c_2}$$

For $Zn_{(s)} + Cl_{2(1\ atm)} \rightarrow Zn^{2+} + 2Cl^-$

$c_1 = [Zn^{2+}]$ and $c_2 = [Cl^-]$

Hence to increase *E*, c_1 should be decreased and c_2 should be increased is $[Zn^{2+}]$ should be decreased and *Cl* should be increased.

121. (c)

Reduction $E_0 M^{3+}/M^{2+}$	Cell reaction		$E_0 M^{2+}/M^{3+}$ (Oxidation)
– .41 *V*	Cr^{2+}	Cr^{3+}	+ . 41 *V*
+ 1.57 *V*	Mn^{2+}	Mn^{3+}	– 1.57 *V*
+ 0.77 *V*	Fe^{2+}	Fe^{3+}	– 0.77 *V*
+ 1.97 *V*	Co^{2+}	Co^{3+}	– 1.97 *V*

As Cr has maximum oxidation potential value, therefore its oxidation should be easiest.

122. (a) $Fe(s) \rightarrow Fe^{2+} + 2e^-$; ΔG^o_1

$2H^+ + 2e^- + \frac{1}{2}O_2 \rightarrow H_2O(l)$; ΔG^o_2

$Fe(s) + 2H^+ + \frac{1}{2}O_2 \rightarrow Fe^{2+} + H_2O$; ΔG^o_3

Applying, $\Delta G^o_1 + \Delta G^o_2 = \Delta G^o_3$

$\Delta G^o_3 = (-2F \times 0.44) + (-2F \times 1.23)$

$\Delta G^o_3 = -(2 \times 96500 \times 0.44 + 2 \times 96500 \times 1.23)$

$\Delta G^o_3 = -322310\ J$

$\therefore\ \Delta G^o_3 = -322\ kJ$

128. (a) $\Delta G^o = -2.303RT\log K_{eq}$ or $\Delta G^o = -nFE^o_{cell}$

129. (a) Any redox reaction would occur spontaneously if the free energy change (ΔG) is negative.

$\Delta G^o = nFE^o$

Where n is the number of electrons involved, F is the value of Faraday and E^o is the cell emf. ΔG^o can be negative if E^o is positive.

Corrosion

2. (d) Rusting of iron is catalysed by $[H^+]$.

3. (d) $HgCl_2$ has corrosive action. It is highly poisonous. It sublimes on heating. It is, therefore, known as corrosive sublimate.

4. (a) $Fe \rightarrow Fe^{2+} + 2e$ (anode reaction)

$O_2 + 2H_2O + 4e \rightarrow 4OH^-$ (cathode reaction)

The overall reaction is

$2Fe + O_2 + 2H_2O \rightarrow 2Fe(OH)_2$

$Fe(OH)_2$ may be dehydrated to iron oxide FeO, or further oxidised to $Fe(OH)_3$ and then dehydrated to iron rust, Fe_2O_3.

Critical Thinking Questions

1. (c) $(126\ scm^2)\ \wedge^0_{NaCl} = \wedge^0_{Na^+} + \wedge^0_{Cl^-}$ .....(1)

$(152\ scm^2)\ \wedge^0_{KBr} = \wedge^0_{K^+} + \wedge^0_{Br^-}$ . ....(2)

$(150\ scm^2)\ \wedge^0_{KCl} = \wedge^0_{K^+} + \wedge^0_{Cl^-}$ . ....(3)

By equation (1)+(2) – (3)

$\therefore\ \wedge^0_{NaBr} = \wedge^0_{Na^+} + \wedge^0_{Br^-}$

$= 126 + 152 - 150 = 128\ Scm^2 mol^{-1}$

2. (a) At cathode : $2H^+_{(aq)} + 2e^- \rightarrow 2H$

$$2H + \frac{1}{2}O_2 \rightarrow H_2O$$

$$2H^+ + \frac{1}{2}O_2 + 2e^- \rightarrow H_2O$$

3. (c) H_2 undergoes oxidation and $AgCl\ (Ag^+)$ undergoes reduction.

4. (b) In this reaction $\underbrace{Fe^{2+} + \overbrace{\overset{0}{Zn} \rightarrow}^{\text{Oxidation}} \overset{2+}{Zn}}_{\text{Reduction}} + \overset{0}{Fe}$

$EMF = E_{cathode} - E_{anode} = -0.41 - (-0.76)$

$EMF = +0.35\ V$.

5. (c) $NO_3^- + 4H^+ + 4e^- \rightarrow 2H_2O + NO$. In this equation all the atoms are balanced. For balancing added $3e^-$ to $L.H.S.$ we have, $NO_3^- + 4H^+ + 3e^- \rightarrow 2H_2O + NO$.

6. (a) $E_{cell} = E^o_{cell} - \frac{0.059}{2}\log\frac{(Zn^{++})}{(Cu^{++})}$

$= 1.10 - \frac{0.059}{2}\log\frac{0.1}{0.1} = 1.10\ V$.

7. (a) The tendency to gain electron is in the order $Z > Y > X$

Thus $Y + e \rightarrow Y^-$; $X \rightarrow X^+ + e$.

8. (b) $E_{OP} = E^o_{OP} - \frac{0.059}{1}\log\frac{[H^+]}{P_{H_2}}$

$\therefore [H^+] = 10^{-10}$; $P_{H_2} = 1\ atm$; $E_{OP} = 0.59\ V$.

9. (a.c,d)Decomposition of H_2O_2 is an example of exothermic reaction, negative catalysis and auto-oxidation.

10. (a) 27 *gm* of *Al* is obtained by passing a current of 3 × 96500 *C*.

∵ 1 *gm* of *Al* is obtained by passing a current of $3 \times \frac{96500}{27} C$.

∴ 5.12 × 10^3 *gm* of *Al* is obtained by passing a current of $3 \times \frac{96500}{27} \times 5.12 \times 1000$

= 1.83 × 10^7 *C* × 3 = 5.49 × 10^7*C*.

11. (c) $\Lambda^{\infty}_{HOAC} = \Lambda^{\infty}_{NaOAC} + \Lambda^{\infty}_{HCl} - \Lambda^{\infty}_{NaCl}$

$= 91.0 + 426.2 - 126.5 = 390.7$

12. (d) $\frac{\omega_1}{E_1} = \frac{\omega_2}{E_2}$; $\frac{\omega_1}{3} = \frac{270}{93}$; $\omega_1 = 90\,kg$.

13. (c) *Eq of* Al = *eq of* H_2

$\frac{4.5}{\frac{27}{3}} =$ *eq of* H_2; $\frac{4.5}{9} =$ *eq of* H_2

$2H^+ + 2e^- \rightarrow H_2$

eq. of H_2 = *Number of moles × n factor*

$0.5 = n_{H_2} \times 2$

$V_{H_2} = \frac{0.5}{2} \times 22.4$; $V_{H_2} = 5.6\ L$

14. (c) The reaction taking place at anode is

$2Cl^- \rightarrow Cl_2 + 2e^-$

1 *mole* 2 × 96500 coulomb

Q = *i* . *t* = 1 × 30 × 60 = 1800 coulomb.

The amount of chlorine liberated by passing 1800 coulomb of electric charge

$= \frac{1 \times 1800 \times 71}{2 \times 96500} = 0.66\ g$.

Assertion & Reason

1. (a) The nature of the cathode can affect the order of discharge of ions.

2. (b) 1 mole of silver = 1*g* equivalent of silver

1 mole of copper = 2*g* equivalent of copper

We know from Faraday's law of electrolysis that "The weight of ion deposited on an electrode is directly proportional to the quantity of electricity passed".

4. (d) Copper is present below hydrogen therefore hydrogen from *HCl* cannot be liberated by treating with copper. Hence assertion is false while reason is true.

5. (d) Copper cannot liberate hydrogen from a dil. *HCl* solutions because it is situated below hydrogen in the reactivity series. Here both assertion and reason are false.

6. (d) The formation of *Zn* is not possible by placing *Cu* plate in $ZnSO_4$ solution because *Zn* is placed above *Cu* in electrochemical series. Therefore, both assertion and reason are false.

7. (e) Electrical conductivity of copper decreases with increase in temperature because the metallic conductivity is due to the motion of electrons. On increasing temperature the motion of electron increases which hinder in conductance of current. Hence, here assertion is false but the reason is true.

8. (a) Dry air is heavier than wet air because the density of dry air is more than water.

9. (e) Copper is present below hydrogen therefore hydrogen from *HCl* cannot be liberated by treating with copper. Hence, assertion is false while reason is true.

10. (a) *K* and *Cs* emit electrons on exposure to light hence, both are used in photoelectric cells . Here, assertion and reason are true and reason is a correct explanation.

12. (b) We know, $R \propto \frac{l}{A}$ or $R = \rho\left(\frac{l}{A}\right)$, where proportionality constant ρ is called resistivity. If $l = 1m$ and $A = 1m^2$, then $R = \rho$ *i.e.* Resistance = Resistivity.

14. (a) According to Kohlrausch law, "Limiting molar conductivity of an electrolyte can be represented as the sum of the individual contributions of the anion and cation of the electrolyte".

15. (c) One Faraday deposite one gram equivalent of the substance.

16. (b) Gold has higher reduction potential than the given metals. Hence $AuCl_3$ will react with these metals.

17. (a) $Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu(s)$

As the time passes, the concentration of Zn^{2+} keeps on increasing while the concentration of Cu^{2+} keeps on decreasing. At the same time voltage of the cell keeps on decreasing. When there is no change in concentration of Cu^{2+} and Zn^{2+} ions, voltmeter gives zero reading and this state is known as equilibrium.

18. (e) A negative value of standard reduction potential means that oxidation takes place on this electrode with reference to *SHE*.

19. (a) A standard cell is one whose *e.m.f.* almost does not change with temperature.

22. (d) Identification of cathode and anode is done by the use of ammeter/voltmeter. Higher is the value of reduction potentials greater would be its oxidising power.

23. (b) If redox reaction is spontaneous, ΔG is –*ve* and hence E^0 is positive. $-\Delta G^0 = nFE^0$ cell

24. (a) Zinc metal which has a more negative electrode potential than iron will provide electrons in preference of the iron, and therefore corrode first. Only when all the zinc has been oxidised does the iron start to rust.

25. (a) Both assertion and reason are true and reason is the correct explanation of assertion.

Anode (oxidation) for eq. $Zn \longrightarrow Zn^{2+} + 2e^-$, so

Excess of electrons and hence negatively charged while cathode is positively charged.

26. (a) Both assertion and reason are true and reason is the correct explanation of assertion.

$$E^0_{Au^{3+}/Au} - E^0_{Ni/Ni^{2+}}$$
$$= 1.50 - (-0.25) = 1.75\,V$$

27. (c) Assertion is true but reason is false. Ions of inert electrolytes are not involved in any electrochemical change until they react chemically with the electrolytes in the two half-cells.

28. (d) Both assertion and reason are false. Potential difference is the difference between the electrode potential of the two electrodes of the cell when cell is under operation while emf is the potential difference generated by a cell when there is zero electron flow.

ELECTROCHEMISTRY

Multiple Choice Questions

1. What is the standard cell potential for the cell

$Zn;Zn^{2+}(1M) \square Cu^{2+}(1M);Cu?$

$(E^{o}\text{for } Zn^{2+}/Zn = -0.76$

$E^{o} \text{ for } Cu^{2+}/Cu = +0.34)$

(a) – 0.76 +(- 0.34)= - 0.42 V (b) - 0.34 +0.76 = + 0.42 V
(c) 0.34 –(- 0.76) = + 1.10 V (d) - 0.76 - (+ 0.34)= -1.10 V

2. The number of electrons involed in the reaction when a Faraday of electricity is passed through an electrolyte in solution is

(a) 12×10^{46} (b) 96540 (c) 8×10^{16} (d) 6×10^{23}

3. Faraday's laws of electrolysis are related to

(a) atomic number of the cation (b) atomic number of anion
(c) equivalent weight of the electrolyte (d) speed of the cation

4. An electrolyte is one

(a)Which conducts electric current in any solvent
(b)Which is capable of ionisation by passing electric current
(c) which dissociates into ions by dissolving in a suitable solvent
(d) none of the above.

5. If same amount of electricity is passed through aqueous solution of $AgNO_3$ and $CuSO_4$ and the number of Ag and Cu atoms deposited are x and y respectively. Then.

(a) x = y (b) x < y (c) y = 2x (d) x = 2y

6. Consider the reaction $M^{n+}(aq) + ne^{-} \rightarrow M(s)$

The standard reduction potential values of the elements M_1, M_2 and M_3 are – 0.34 V, - 3.05 V and – 1.66 V respectively, The order of their reducing power will be

(a) $M_1 > M_2 > M_3$ (b) $M_3 > M_2 > M_1$ (c) $M_1 > M_3 > M_2$ (d) $M_2 > M_3 > M_1$.

7. In the electrolysis of NaCI:

(a) Cl^{-} is oxidized at anode (b) Cl^{-} is reduced at anode
(c) Cl^{-} is oxidized at cathode (d) Cl^{-} is neither reduced nor oxidised

8. When a solution of an electrolyte is heated, the conductance of the solution.

(a) increases because number of molecules of the electrolyte increases
(b) decreases because of the increased heat
(c) decreases because the dissociation of the electrolyte is suppressed
(d) increases because the electrolyte is dissociated more .

9. The number of faradays required to deposit 1 g equivalent of aluminium (At. Wt. = 27) from a solution of aluminium chloride will be
(a) 1 (b) 2 (c) 3 (d) 4.

10. The amount of electricity that can deposit 108 g of silver from silver nitrate solution is
(a) 1 Ampere (b) 1 Coulomb (c) 1 Faraday (d) 2 Ampere.

11. Four alkali metals A, B, C and D are having respectively standard electrode potentials as -3.05, - 1.66, - 0.40 and 0.80 V.which one will be the most reducing.
(a) A (b) B (c) C (d) D.

12. The standard reduction potential values of the three metallic cations X,Y and Z are 0.52, – 3.03 and – 1.18 V respectively. The order of reducing power of the corresponding metals is
(a) Y > Z > X (b) X > Y >Z (c) Z > Y > X (d) Z > X > Y.

13. For the electrochemical cell, $M|M^+||X^-|X$,
$E^\circ(M^+/M) = 0.44V$ and $E^\circ(X/X^-) = 0.33V$
From this data, one can deduce that
(a) $M + X \rightarrow M^+ + X^-$ is the spontaneous reaction
(b) $M^+ + X^- \rightarrow M + X$ is the spontaneous reaction
(c) $E_{cell} = 0.77V.$
(d) $E_{cell} = -0.77V.$

14. The relationship between stardard reduction potential of a cell and equilibrium constant is shown by
(a) $E^0_{cell} = \frac{n}{0.059}\log K_c$ (b) $E^0_{cell} = \frac{0.059}{n}\log K_c$
(c) $E^0_{cell} = 0.059n\log K_c$ (d) $E^0_{cell} = \frac{\log K_c}{n}$

15. If 0.01M solution of an electrolyte has a resistance of 40 ohms in a cell having a cell constant of 0.4 cm^{-1} then its molar conductance in ohm^{-1} cm^2 mol^{-1} will be
(a) 10^4 (b) 10^3 (c) 10^2 (d) 10.

16. Specific conductance of 0.1M Nitric acid is 6.3×10^{-2} Ohm^{-1} cm^{-1}. The molar conductance of the solution is
(a) 630 ohm^{-1} cm^2 (b) 315 ohm^{-1} cm^2
(c) 100 ohm^{-1} cm^2 (d) 6300 ohm^{-1} cm^2

17. What weight of copper will be deposited by passing 2 faradays of electricity through a cupric salt (At. wt. of Cu= 63.5)?

(a) 2.0 g (b) 3.175g (c) 63.5g (d) 127.0g

18. When 9650 coulombs of electricity is passed through a solution of copper sulphate, the amount of copper deposited is (Given At.wt. of cu = 63.6)
(a) 0.318 g (b) 3.18 g (c) 31.8 g (d) 63.6g

19. A solution of $CuSO_4$ is electrolysed for 7 minutes with a current of 0.6 ampere. The amount of electricity passed is equal to
(a) 4.2 columbs (b) 2.6×10^{-3} Faraday
(c) 126 Coulombs (d) 35 Coulombs

20. When an electric current is passed through acidulated water, 112 ml of hydrogen gas at NTP is collected at the cathode in 965 seconds.The current passed in amperes, is
(a) 1.0 (b) 0.5 (c) 0.1 (d) 2.0.

21. How long will it take for a current of 3 amperes to decompose 36 g of water?(Eq. wt of hydrogen is 1 and that of oxygen 8)
(a) 36 hours (b) 18 hours(c) 9 hours (d) 4.5 hours

22. Four moles of electrons were transferred from anode to cathode in an experiment on electrolysis of water. The total volume of the two gases (dry and at STP) produced will be approximately (in litres)
(a) 22 .4 (b) 44.8 (c) 67.2 (d) 89.4

23. Calculate the weight of copper that will be deposited at the cathode in the electrolysis of a 0.2 M solution of copper sulphate when quantity of electricity equal to that required to liberate $2.24l$ of hydrogen at NTP from a 0.1 M aqueous sulphuric acid, is passed. (Atomic mass of Cu = 63.5)
(a) 1.59 g (b) 6.35 g (c) 3.18 g (d) 12.70 g.

24. How many coulombs of electricity are required for reduction of 1 mole of MnO_4^- to Mn^{2+}?
(a) 96500 C (b) 1.93×10^5C (c) 4.83×10^5C (d) 9.65×10^6C

25. The same amount of electricity was passed through two separate electrolytic cells containing solutions of nickel nitrate and chromium nitrate respectively. If 0.3 g of nickel was deposited in the first cell, the amount of chromium deposited is (At wt. Ni= 59, Cr= 52)
(a) 0.1 g (b) 0.17 g (c) 0.3 g (d) 0.6 g.

26. How much quanitity of electricity has to be passed through 200 ml of 0.5 M $CuSO_4$ solution to completely deposit copper
(a) 96500 C (b) $2\times9650C$ (c) $2\times96500C$ (d) $4\times96500C$

27. How many atoms of hydrogen are liberated at cathode , when 965 coulombs of charge is passed through water?

(a) 6.02×10^{21} (b) 6.02×10^{23} (c) 6.02×10^{19} (d) $\frac{1}{6.02} \times 10^{23}$

28. An electric current is passed through silver voltameter connected to a water voltameter. The cathode of the silver voltameter weighed 0.108 g more at the end of the electrolysis. The volume of oxygen evolved at STP is
(a) 56 cm^3 (b) 550 cm^3 (c) 5.6 cm^3 (d) 11.2 cm^3 (e) 22.4 cm^3

29. The emf of the cell $Ni/Ni^{2+}(1.0M)\,\|\,Au^{3+}(1.0M)/Au$ is
E° for $Ni^{2+}/Ni = -0.25$ V; E° for $Au^{3+}/Au = 1.5$ V]
(a) + 1.25 V (b) +1.75 V (c) -1.25 V (d) -1.75 V

30. The potential of the cell containing two hydrogen electrodes as represented below
$Pt, H_2(g)\left|H^+(10^{-6}M)\right\|H^+(10^{-4}M)\big|\,H_2(g), Pt$ at 298 K is
(a) -0.118 V (b)-0.0591V (c) 0.118 V (d) 0.0591 V.

31. The e.m.f of the following Daniell cell at 298 K is E_1
$Zn\left|ZnSO_4(0.01M)\right\|CuSO_4(1.0M)\big|Cu$ When the concentration of $ZnSO_4$ is 1.0 M and that of $CuSO_4$ is 0.01 M, the e.m.f changed to E_2.
What is the relationship between E_1 and E_2 ?
(a) $E_1 > E_2$ (b) $E_1 < E_2$ (c) $E_1 = E_2$ (d) $E_2 = 0 \neq E_1$

32. If the standard electrode potential of Cu^{2+}/Cu electrode is 0.34 V, what is the electrode potential of 0.01 M concentration of Cu^{2+}? (T= 298 K)
(a) 0.399 V (b) 0.281 V (c) 0.222V (d) 0.176 V.

33. The standard reduction potential for Cu^{2+}/Cu is + 0.34V. The reduction potential at pH= 14 for the above couple is $\{Cu^{2+}]$ at pH 14 is $10^{-19}\}$
(a) -0.22 V (b) +0.22V (c) -0.34 V (d) +0.34V

34. A current of 12 ampere is passed through an electrolytic cell containing aq. $NiSO_4$ solution. Both Ni and H_2 gas are formed at the cathode. The current efficiency is 60%. What is the mass of nickel deposited on the cathode per hour? (At. wt. of Ni = 98 .7)
(a) 7.883 gm (b) 3.941 gm (c) 5.91 gm (d) 2.645 gm

35. Consider the following statements pertaining to fuel cells:
1. Hydrogen-Oxygen fuel cell makes use of con KOH solution as electrolyte and porous graphite impregnated with platinum as electrodes .
2. The efficiency of the fuel cell is less than unity due to plarisation at electrodes and the resistance offered by the electrode and the electrolyte.

3. The electrical work, assuming the cell to be working reversibly may be represented as $-\Delta G = W_{elec} = -\Delta H + T\Delta S$

Which of the above statements are correct ?

(a) 1 and 2 (b) 1 and 3 (c) 2 and 3 (d) 1, 2 and 3

ELECTROCHEMISTRY

Answer key

Q.	Ans.	Q.	Ans.	Q.	Ans.	Q.	Ans.
1.	C	11.	A	21.	A	31.	A
2.	D	12.	A	22.	C	32.	B
3.	C	13.	B	23.	B	33.	A
4.	C	14.	B	24.	C	34.	A
5.	D	15.	B	25.	B	35.	D
6.	D	16.	A	26.	B		
7.	A	17.	C	27.	A		
8.	D	18.	B	28.	C		
9.	A	19.	B	29.	B		
10.	C	20.	A	30.	C		

Solution : -

1. Cell potential

$$= E^o_{Red}(RHS) - E^o_{Red}(LHS)$$

$$= 0.34 – (-0.76) = +1.10 \text{ V.}$$

2. 1 F = Avogadro's no. of electrons.

3. Faraday's laws are related to equivalent weights

4. An electrolyte dissociates into ions when dissolved in suitable solvent.

5. $Ag^+ + e^- \rightarrow Ag$, $Cu^{2+} + 2\ e^- \rightarrow Cu$. Thus same quantity of electricity wil deposit double the no. of Ag atoms than Cu i. e. x = 2 y.

6. Less the reduction potential, greater is the reducing power.

7. Cl^- ion is oxidized at anode.

8. Conductance of electrolytic solution increases with temperature because dissociation increases.

9. To deposit 1 g eq. of any element, 1 F is required.

10. 108 g Ag = 1 g eq. of Ag. It requires 1 F.

11. Lower the reduction potential, stronger is the reducing agent.

12. Greater the reduction potential, less is the reducing power.

13. EMF for (b) is positive and = $E^0_{Red}(M) + E^o_{ox}(X)$

$= 0.44 + (-0.33) = 0.11$ V.

14. $E^0_{cell} = \frac{0.0591}{n} \log K_c$.

15. $K = \frac{1}{R} \times \text{cell const} = \frac{0.4}{40} = 10^{-2}$

$\wedge_m = \frac{K \times 1000}{\text{Molarity}} = \frac{10^{-2} \times 1000}{10^{-2}} = 1000 = 10^3 \text{ohm}^{-1}\ \text{cm}^2\ \text{mol}^{-1}$

16. $\wedge_m = \frac{1000 \times K}{\text{Molarity}} = \frac{1000 \times 6.3 \times 10^{-2}}{0.1}$ = 630 $\text{ohm}^{-1}\ \text{cm}^2$.

17. $Cu^{2+} + 2e^- \rightarrow Cu$.

2 F will deposit Cu = 1 g atom = 63.5 g.

18. 2×96500 C deposit Cu = 63.6 g. Hence 9650 C will deposit Cu = 3.18 g.

19. $Q = C \times t = 0.6 \times (7 \times 60) = 252C$, $= 252/96500F - = 2.6 \times 10^{-3} F$.

20. 1 g eq. of H_2 i. e. 1 g or 11200 cc is obtained from 96500 C

21. Eq. Wt of H_2O =1+8 = 9. Hence 9 g is decomposed by 96500 C.

So 36 g will be decomposed by

Q = 96500 × 4 C.

Hence t = $\frac{Q}{I} = \frac{96500 \times 4}{3}$ s = 35.7 hrs □ 36 hrs.

22. $H_2O \rightarrow H_2 + \frac{1}{2}O_2$ or $2H^+ + 2e^- \rightarrow H_2$

i.e, 2 moles of e^- produce 1 mole of H_2 *i.e*, 22.4 L.

Hence 4 moles of e^- will give H_2 = 44.8L

O_2 produced = $\frac{1}{2}$ of $H_2 = 22.4L$

Total volume = 44.8 + 22.4 = 67.2 L.

23. 2.24 L of H_2 at NTP = 0.2 g of H_2

$\frac{Wt\ of\ cu}{Wt\ of\ H_2} = \frac{Eq.\ Wt.\ of\ Cu}{Eq.\ Wt.\ of\ H}$ i.e. $\frac{\text{Wt of cu}}{0.2} = \frac{63.5/2}{1}$

or wt . of Cu = 6.35 g.

24. $(MnO_4)^{-1} \rightarrow Mn^{2+}$ i.e. $Mn^{7+} + 5e^- \rightarrow Mn^{2+}$.

Thus 1 mole of MnO_4^- requires 5 F

= $5 \times 96500C = 482500 \approx 4.83 \times 10^5 C.$

25. $\frac{\text{Wt. of Ni}}{\text{wt. of Cr}} = \frac{\text{Eq. Wt. of Ni}}{\text{Eq. wt. of Cr}}, \frac{0.3}{\text{Wt.of Cr}} = \frac{59/2}{52/3}$ or Wt. of Cr $= 0.17$ g

26. 200 ml of 0.5 M $CuSO_4$ contains
$CuSO_4$ = 0.1 mole.
$Cu^{2+} + 2e^- \rightarrow Cu$
To deposit 0.1 mole of Cu^{2+}, electricity required = $2 \times 9650C$

27. $H_2O \rightarrow H_2 + \frac{1}{2}O_2$ or $2H^+ + 2e^- \rightarrow 2H$

i.e, 96500 C produce 1 mole of H-atoms $= 6.02 \times 10^{23}$ atoms. So 965 C will produce H – atoms = 6.02×10^{21}.

28. $$\frac{\text{wt.of silver deposited}}{\text{Wt. of } O_2 \text{ produced}} = \frac{\text{Eq.wt.ofAg}}{\text{Eq.Wt.of oxygen}}$$

$$\frac{0.108}{\text{Wt. of } O_2 \text{ produced}} = \frac{108}{8}$$

$\therefore$ Wt. of O_2 produced $= 8 \times 10^{-3}$ g

$\therefore$ Vol of O_2 produced at STP $= \frac{22400}{32} \times 8 \times 10^{-3} = 5.6 cm^3$

29. $E^0_{cell} = E^0_{Red}(RHS) - E^0_{Red}(LHS) = 1.5 - (0.25) = 1.75V.$

30. This is a concentration cell.

$$E^o_{cell} = \frac{0.059}{n}\log\frac{C_2}{C_1} = \frac{0.059}{1}\log\frac{10^{-4}}{10^{-6.}}$$

31. For the given cell, $Zn + Cu^{2+} \rightarrow Zn^{2+} + Cu$

$$E = E^0 - \frac{0.0591}{2}\log\frac{[Zn^{2+}]}{[Cu^{2+}]}$$

$$E_1 = E^0 - \frac{0.0591}{2}\log\frac{0.01}{1.0}$$

$$E_2 = E^0 - \frac{0.0591}{2}\log\frac{1.0}{0.01}$$ Thus $E_1 > E_2.$

32. $Cu^{2+} + 2e^- \rightarrow Cu.$

$$E = E^0 - \frac{0.0591}{n}\log\frac{1}{[Cu^{2+}]} = 0.34 - \frac{0.0591}{2}\log\frac{1}{0.01}$$

= 0.2809 = 0.281 V.

33. $Cu^{2+} + 2e^- \rightarrow Cu$, $E = E^0 - \frac{0.059}{2}\log\frac{1}{[Cu^{2+}]}$

$= 0.34 - \frac{0.059}{2} \log \frac{1}{10^{-19}} = -0.22\text{V}$

34. $Q = 12 \times 60 \times 60 = 43200\text{C}$

$\text{Ni}^{2+} + 2e^{-} \rightarrow \text{Ni}$, Theoretically $2 \times 96500\text{C}$ will deposit Ni = 58.7 g.
Hence 43200C will deposit Ni = 13.137 g. As current efficiency
is 60 %. Mass actually deposited = $\frac{60}{100} \times 13.137 = 7.88\text{g}$

35. All the given statements about the fuel cells are correct.

Electrochemistry

SET Self Evaluation Test - 12

1. The mass of copper deposited from a solution of $CuSO_4$ by passage of 5 *A* current for 965 second is (*Mol*. *wt*. of Copper = 63.5) **[AIIMS 2001]**

(a) 15.875 *g* (b) 1.5875 *g*

(c) 4825 *g* (d) 96500 *g*

2. The current in a given wire is 1.8 *A*. The number of coulombs that flow in 1.36 minutes will be **[AIIMS 2001]**

(a) 100 *C* (b) 147 *C*

(c) 247 *C* (d) 347 *C*

3. A solution of a salt of a metal was electrolysed for 150 *minutes* with a current of 0.15 *amperes*. The weight of metal deposited was 0.783 *gm*. The equivalent weight of the metal is **[AFMC 2001]**

(a) 55.97 *gm* (b) 65.97 *gm*

(c) 75.97 *gm* (d) 85.97 *gm*

4. The resistance of 0.01*N* $NaCl$ solution at $25^o C$ is 200 Ω. Cell constant of conductivity cell is 1 cm^{-1}. The equivalent conductance is **[CBSE PMT 1999]**

(a) $5 \times 10^2 \Omega^{-1} cm^2 eq^{-1}$ (b) $6 \times 10^3 \Omega^{-1} cm^2 eq^{-1}$

(c) $7 \times 10^4 \Omega^{-1} cm^2 eq^{-1}$ (d) $8 \times 10^5 \Omega^{-1} cm^2 eq^{-1}$

5. Which of the following reaction is possible at anode **[AIEEE 2002]**

(a) $2Cr^{3+} + 7H_2O \rightarrow Cr_2O_7^{2-} + 14H^+$

(b) $F_2 \rightarrow 2F^-$

(c) $\frac{1}{2}O_2 + 2H^+ \rightarrow H_2O$

(d) None of these

6. What is the standard cell potential for the cell $Zn/Zn^{2+}(1M) || Cu^{2+}(1M)/Cu$ E^0 for $Zn/Zn^{2+}(1M) = -0.76V$ & $Cu^{2+}/Cu = +0.34V$ **[AIIMS 1980]**

(a) $-0.76 + (-0.34) = -0.42V$

(b) $-0.34 + 0.76 = +0.42V$

(c) $0.34 - (-0.76) = 1.10V$

(d) $-0.76 - (+0.34) = -1.10V$

7. Normal aluminium electrode coupled with normal hydrogen electrode gives an emf of $1.66 volts$. So the standard electrode potential of aluminium is **[KCET 1987]**

(a) – 1.66 *V* (b) + 1.66 *V*

(c) – 0.83 *V* (d) + 0.83 *V*

8. Which one among the following is the strongest reducing agent

$Fe^{2+} + 2e^- \rightarrow Fe(-0.44V)$

$Ni^{2+} + 2e^- \rightarrow Ni(-0.25V)$

$Sn^{2+} + 2e^- \rightarrow Sn(-0.14V)$

$Fe^{3+} + e^- \rightarrow Fe^{2+}(-0.77V)$

[BHU 1998]

(a) Fe (b) Fe^{2+}

(c) Ni (d) Sn

9. The cell reaction of the galvanic cell $Cu_{(s)} | Cu^{2+}{}_{(aq)} || Hg^{2+}{}_{(aq)} | Hg_{(l)}$ is **[EAMCET 2003]**

(a) $Hg + Cu^{2+} \rightarrow Hg^{2+} + Cu$

(b) $Hg + Cu^{2+} \rightarrow Cu^+ + Hg^+$

(c) $Cu + Hg \rightarrow CuHg$

(d) $Cu + Hg^{2+} \rightarrow Cu^{2+} + Hg$

10. The specific conductivity of *N*/10 KCl solution at $20^o C$ is $0.0212 ohm^{-1} cm^{-1}$ and the resistance of cell containing this solution at $20^o C$ is 55 *ohm*. The cell constant is

[AIIMS 1999]

(a) 1.166 cm^{-1}

(b) 2.173 cm^{-1}

(c) 3.324 cm^{-1}

(d) 4.616 cm^{-1}

11. The oxide which is not reduced by hydrogen is

[JIPMER 1999]

(a) Ag_2O (b) K_2O

(c) Fe_2O_3 (d) P_4O_{10}

Answers and Solutions

(SET -12)

1. (b) Current (I) = 5A and time (t) = 965 *sec*.

We know that equivalent weight of copper $= \frac{\text{Molecular weight}}{\text{Valancy}} = \frac{63.5}{2}$ and quantity of electricity passed in coulomb = current × time = 5 × 965 = 4825*C*. Since 96500 *coulombs* will deposit $\frac{63.5}{2} g$ of copper therefore 4825 coulombs will deposit

$= \frac{63.5 \times 4825}{96500 \times 2} = 1.5875 g$.

2. (b) $Q = I \times t$; $1.8 \times 1.36 \times 60 = 147C$.

3. (a) Time (t) = 150 *min* = 9000 *sec*

Current (I) = 0.15 *A*

Weight of metal (w) = 0.783 *g*.

We know $Q = I \times t = 0.15 \times 9000 = 1350C$.

Since 1350 *C* of electricity will deposited 0.783 *g* of metal, so, 96500 *C* of electricity will deposited

$\frac{0.783 \times 96500}{1350} = 55.97 g$.

4. (a) $\lambda = k \times V = \frac{1}{R} \times \frac{l}{a} \times V = \frac{1}{200} \times 1 \times 10{,}000$

$= 5 \times 10^2 \Omega^{-1} cm^2 eq.^{-1}$

5. (a) Oxidation always occurs at anode.

6. (c) $E^o = E_{\text{cathode}} - E_{\text{anode}}$

$E^o = 0.34 - (-0.76)$; $E^o = 1.10\ volt$.

7. (a) $E^o_{\text{cell}} = 1.66 = E^o_{H^+/H_2} - E^o_{Al^{3+}/Al}$

$= O - E^o_{Al^{3+}/Al}$ or $E_{Al^{3+}/Al} = -1.66V$.

8. (a) The reduction potential of *Fe* is very high, so it is a strongest reducing agent.

9. (b) $\underset{\text{anode oxidation}}{Cu_{(s)} | Cu^{2+}_{(Ag)}} || \underset{\text{cathode reduction}}{Hg^{2+}_{(Ag)} | Hg_{(l)}}$

Reduction

$Cu + Hg^{2+} \rightarrow Cu^{2+} + Hg$.

Oxidation

10. (a) $K = \frac{1}{R} \times$ cell constant

$= K \times R = 0.0212 \times 55 = 1.166\ cm^{-1}$.

11. (b) On the basis of electrochemical series K_2O is not reduced by hydrogen.

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Chemical Equilibrium

Level - 1

Multiple Choice Questions

1. If $\Delta n (= n_p - n_r)$ is the change in the number of moles of gaseous substances during a reaction, then equilibrium constants K_p and K_c are related as

   (a) $K_p = K_c(RT)^{-\Delta n}$ (b) $K_c = K_p(RT)^{-\Delta n}$

   (c) $K_p = (RT)^{\Delta n}/K_c$ (d) $K_p - K_c = (RT)^{\Delta n}$

2. The relation between K_p and K_c for the reaction $2NO(g) + Cl_2(g) \rightleftharpoons 2NOCl(g)$ is

   (a) $K_p = K_c$ (b) $K_p = K_c(RT)$ (c) $K_p = K_c/RT$ (d) $K_p = K_c/(RT)^2$

3. The ratio of K_p/K_c for the reaction: $CO(g) + 1/2O_2(g) \rightleftharpoons CO_2(g)$ is:

   (a) 1 (b) RT (c) $(RT)^{1/2}$ (d) $(RT)^{-1/2}$

4. For a homogeneous chemical reaction, $K_p = K_c$ when

   (a) $\Delta n = 0$ (b) $\Delta n = 1$ (c) $\Delta n = 2$ (d) $\Delta n = \infty$.

5. Consider the equilibrium reactions,

   $H_3PO_4 \overset{K_1}{\rightleftharpoons} H^+ + H_2PO_4^-$

   $H_2PO_4^- \overset{K_2}{\rightleftharpoons} H^+ + HPO_4^{-2}$

   $HPO_4^{-2} \overset{K_3}{\rightleftharpoons} H^+ + PO_4^{-3}$

   The equilibrium constant, K for the following dissociation

   $H_3PO_4 \rightleftharpoons 3H^+ + PO_4^{-3}$ is

   (a) K_1/K_2K_3 (b) $K_1K_2K_3$ (c) K_2/K_1K_3 (d) $K_1 + K_2 + K_3$

6. If K_1 and K_2 are the equilibrium constants of the equilibria (i) and (ii) respectively, what is the relationship between the two constants?

   (i) $SO_2(g) + \frac{1}{2}O_2(g) \rightleftharpoons SO_3(g); K_1$ (ii) $2SO_3(g) \rightleftharpoons 2SO_2(g) + O_2(g); K_2$

   (a) $(K_1)^2 = \frac{1}{K_2}$ (b) $K_2 = (K_1)^2$ (c) $K_1 = \frac{1}{K_2}$ (d) $K_1 = K_2$.

7. What will be the equilibrium constant at 717 K for the reaction:

   $2HI(g) \rightleftharpoons \frac{1}{2}H_2(g) + \frac{1}{2}I_2(g)$

   If its value for the reaction $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$ at 717 K is 64 ?

   (a) 64 (b) 8 (c) 1/64 (d) 1/8

8. For the system $2A(g)+B(g) \rightleftharpoons 3C(g)$, the expression for the equilibrium constant K is

(a) $\frac{2[A]\times[B]}{[3C]}$ (b) $\frac{[A]\times[B]}{[C]^2}$ (c) $\frac{[3C]}{[2A]\times[B]}$ (d) $\frac{[C]^3}{[A]^2[B]}$

9. Starting with one mole of O_2 and two moles of SO_2, the equilibrium for the formation of SO_3 was established at a certain temperature. If V is the volume of the vessel and $2x$ is the number of moles of SO_3 present, the equilibrium constant will be

(a) $\frac{x^2V}{(1-x)^3}$ (b) $\frac{4x^2}{(2-x)(1-x)}$ (c) $\frac{(1-x)^3}{2V}$ (d) $\frac{x^2}{(2-x)(1-x)}$

10. The equilibrium constant, K_p for the reaction $A \rightleftharpoons 2B$ is related to degree of dissociation α of A and total pressure P as

(a) $\frac{4\alpha^2P}{1-\alpha^2}$ (b) $\frac{4\alpha^2P^2}{1-\alpha^2}$ (c) $\frac{4\alpha^2P^2}{1-\alpha}$ (d) $\frac{4\alpha^2P}{1-\alpha}$

11. For the reaction, $Cu(s) + 2Ag^+(aq) \rightleftharpoons Cu^{2+}(aq) + 2Ag(s)$ the equilibrium constant K_c is given by

(a) $\frac{[Cu^{2+}][Ag]^2}{[Cu][Ag^+]^2}$ (b) $\frac{[Cu^{2+}][2Ag]}{[Cu][2Ag^+]}$ (c) $\frac{[Cu^{2+}]}{[Ag^+]^2}$ (d) $\frac{[Ag^+]^2}{[Cu^{2+}]}$

12. For the reaction $2A(g) + B(g) \rightleftharpoons 3C(g) + D(g)$
two moles each of A and B were taken into a flask. The following must always be true when the system attained equilibrium

(a) [A] = [B] (b) [A] < [B] (c) [B] = [C] (d) [A] > [B]

13. In which of the following reactions the equilibrium constant will have no units?

(a) $NO(g) \rightleftharpoons \frac{1}{2}N_2(g) + \frac{1}{2}O_2(g)$ (b) $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$

(c) $CO(g) + H_2O(g) \rightleftharpoons CO_2(g) + H_2(g)$ (d) In all the above relations.

14. Consider the reaction $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$ in a closed container at equilibrium. At a fixed temp. what will be the effect of adding more PCl_5 on the equilibrium concentration of Cl_2 (g)?

(a) it decreases (b) it increases

(c) it remains unaffected

(d) it cannot be predicted without the value of K_p.

15. In which of the following reaction, pressure has no effect on equilibrium?

(a) $N_2O_4(g) \rightleftharpoons 2NO_2(g)$ (b) $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$

(c) $CO_2(g) + H_2(g) \rightleftharpoons CO(g) + H_2O(g)$ (d) $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$.

16. Which of the following reactions will be favoured at low pressure?
(a) $N_2 + O_2 \rightleftharpoons 2NO$ (b) $H_2 + I_2 \rightleftharpoons 2HI$
(c) $PCl_5 \rightleftharpoons 2PCl_3 + Cl_2$ (d) $N_2 + 3H_2 \rightleftharpoons 2NH_3$

17. For the manufacture of ammonia by Haber's process, i.e.
$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g), \Delta H = -22\,\text{kcal}$ the favourable conditions are
(a) High temperature, high pressure
(b) Low temperature, low pressure
(c) High temperature, low pressure
(d) Low temperature, high pressure.

18. For a hypothetical reaction of the kind $AB_2(g) + \frac{1}{2}B_2(g) \rightleftharpoons AB_3(g); \Delta H = -xkJ$
More AB_3 could be produced at equilibrium by
(a) using a catalyst (b) removing some of B_2
(b) increasing the temperature (d) increasing the pressure.

19. For the reaction, $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$, the equilibrium constant K_p changes with
(a) Total pressure (b) Catalyst
(c) The amounts of H_2 and I_2 present (d) Temperature.

20. The equilibrium constant in a reversible chemical reaction at a given temperature
(a) depends on the initial concentration of the reactants
(b) depends on the concentration of one of the products at equilibrium
(c) does not depend on the initial concentrations of reactants
(d) is not characteristic of the reaction.

21. A liquid is in equilibrium with its vapour at its boiling point. On the average, the molecules in the two phases have equal
(a) Intermolecules forces (b) Potential energy
(b) Kinetic energy
(c) Both kinetic energy and potential energy.

22. k_1 and k_2 are the velocity constants of forward and backward reactions. The equilibrium constant K of the reaction is:
(a) $k_1 \times k_2$ (b) $k_1 - k_2$ (c) $\frac{k_1}{k_2}$ (d) $\frac{k_1 + k_2}{k_1 - k_2}$

23. Select the reaction for which the equilibrium constant is written as

$[MX_3]^2 = K[MX_2]^2[X_2]$

(a) $MX_3 \rightleftharpoons MX_2 + \frac{1}{2}X_2$ (b) $2MX_3 \rightleftharpoons 2MX_2 + X_2$

(c) $2MX_2 + X_2 \rightleftharpoons 2MX_3$ (d) $MX_2 + \frac{1}{2}X_2 \rightleftharpoons MX_3$.

24. k_1 and k_2 are equilibrium constant for reactions (1) and (2)

$N_2(g) + O_2(g) \rightleftharpoons 2NO(g)....(1)$ $NO(g) \rightleftharpoons \frac{1}{2}N_2(g) + \frac{1}{2}O_2(g)....(2)$

Then,

(a) $K_1 = \left(\frac{1}{K_2}\right)^2$ (b) $K_1 = K_2^2$ (c) $K_1 = \frac{1}{K_2}$ (d) $K_1 = (K_2)^o$

25. In which of the following case, does the reaction go farthest to completion?
(a) $K = 10^2$ (b) $K = 10$ (c) $K = 10^{-2}$ (d) $K = 1$

26. For the reaction $2A + B \rightleftharpoons C, \Delta H = +x$ Cals,
Which one of the following conditions would favour the yield of C on the basis of Le Chatelier principle?
(a) High pressure, high temperature (b) Only low temperature
(c) High pressure, low temperature (d) Only low pressure.

27. At a certain temperature, the following reactions:
$NO(g) + 1/2O_2(g) \rightleftharpoons NO_2(g)$, $NO_2(g) + NO(g) \rightleftharpoons N_2O_3(g)$ have equilibrium constants K_1 and K_2 respectively. The equilibrium constant for the reaction:
$2NO(g) + 1/2O_2(g) \rightleftharpoons N_2O_3(g)$ at the same temperature would be
(a) $K_1 + K_2$ (b) K_1/K_2 (c) K_2/K_1 (d) K_1K_2

28. In the two gaseous reactions (i) and (ii), at 25⁰C
(i) $NO(g) + 1/2O_2(g) \rightleftharpoons NO_2(g), K_1$ (ii) $2NO_2(g) + \rightleftharpoons 2NO(g) + O_2(g), K_2$
the equilibrium constants K_1 and K_2 are related as
(a) $K_2 = 1/K_1$ (b) $K_2 = K_1/2$ (c) $K_2 = 1/K^2$ (d) $K_2 = K^2$

29. For a chemical reaction $2A + B \rightleftharpoons C$, the thermodynamic equilibrium constant K_p is
(a) in atm^{-2} (b) in atm^{-3} (c) in atm^{-1} (d) dimensionless.

30. Which of the following gives blood red colour with KCNS?
(a) Cu^{2+} (b) Fe^{3+} (c) Al^{3+} (d) Zn^{2+}.

31. The decompsotion of N_2O_4 to NO_2 is carried out at 280° in chloroform. When equilibrium is reached 0.2 mol of N_2O_4 and 2×10^{-3} mol of NO_2 are present in 2 litre solution. The equilibrium constant for the reaction N_2O_4 □ $2NO_2$ is
(a) 1×10^{-3} (b) 2×10^{-3} (c) 1×10^{-5} (d) 2×10^{-5}

32. 1.1 mol of A is mixed with 2.2 mol of B and the mixture is kept in a one-litre flask till the equilibrium, A + 2B □ 2C + D is reached. At equilibrium 0.2 mol of C is formed. The equilibrium constant of the above reaction is
(a) 0.002 (b) 0.004 (c) 0.001 (d) 0.003

33. 1 mol of A and 0.5 mol of B were enclosed in a three litre vessel. The following equilibrium was established under suitable conditions $A + 2B$ □□□ C
At equilibrium, the amount of B was found to be 0.3 mol. the equilibrium constant K_c at the experimental temperature will be
(a) 11.1 (b) 1.11 (c) 0.01 (d) 2.50

34. 1 mole of hydrogen and 2 moles of iodine are taken initially in a 2 litre vessel. The number of moles of hydrogen at equilibrium is 0.2. Then the number of moles of iodine and hydrogen iodide at equilibrium are
(a) 1.2, 1.6 (b) 1.8, 1.0 (c) 0.4, 2.4 (d) 0.8, 2.0

35. The degree of dissociation of dinitrogen tetroxide $N_2O_4(g) \rightarrow 2NO_2(g)$ at temperature T and total pressure P is α. Which one of the following is the correct expression for the equilibrium constant (K_p) at this temperature?
(a) $2\alpha/(1-\alpha^2)$ (b) $\alpha^2P/(1-\alpha)$ (c) $4\alpha^2/(1-\alpha^2)$ (d) $4\alpha^2P/(1-\alpha^2)$

Level – 2

More than one option is correct.

1. Which of the following statements are incorrect?
   (a) For a closed system, S is always maximum at equilibrium.
   (b) The addition of a reactant gas to an ideal-gas reaction mixture shifts the equilibrium in such a way that some of the added gas is used up.
   (c) In any closed system, G is always minimum at equilibrium.
   (d) In the limit $T \to 0$, ΔG^0 approaches ΔH^0

2. The expression for the equilibrium constant for an ideal-gas reaction mixture is given by
   (a) $\frac{d \ln K_c^0}{dT} = \frac{\Delta U^0}{RT^2}$
   (b) $\left(\frac{\partial \ln K_x^0}{\partial T}\right)_p = \frac{\Delta S^0}{RT^2}$
   (c) $\left(\frac{\partial \ln K_x^0}{\partial p}\right)_T = -\frac{\Delta n/\text{mol}}{p}$
   (d) $\frac{d \ln K_p^0}{dT} = \frac{\Delta H^0}{RT^2}$

3. The condition for spontaneity in a chemical reaction is
   (a) $(\Delta G)_{T,p} \le 0$ (b) $(\Delta U)_{S,V} \le 0$ (c) $(\Delta H)_{S,p} \le 0$ (d) $(\Delta S)_{U,V} \ge 0$

4. In which of the following reactions is $K_p < K_c$?
   (a) $CO(g) + Cl_2(g) \rightleftharpoons COCl_2(g)$
   (b) $CO(g) + 3H_2(g) \rightleftharpoons CH_4(g) + H_2O(g)$
   (c) $2BrCl(g) \rightleftharpoons Cl_2(g) + Br_2(g)$
   (d) $I_2(g) \rightleftharpoons 2I(g)$

5. The dissociation of phosgene, which occurs according to the reaction $COCl_2(g) \rightleftharpoons CO(g) + Cl_2(g)$ is an endothermic process. Which of the following will increase the degree of dissociation of $COCl_2$?
   (a) Adding Cl_2 to the system
   (b) Adding helium to the system
   (c) Decreasing the temperature of the system
   (d) Reducing the total pressure

6 The equilibrium of which of the following reactions will not be disturbed by the addition of an inert gas at constant volume?
   (a) $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$
   (b) $N_2O_4(g) \rightleftharpoons 2NO_2(g)$
   (c) $CO(g) + 2H_2(g) \rightleftharpoons CH_3OH(g)$
   (d) $C(s) + H_2O(g) \rightleftharpoons CO(g) + H_2(g)$

7. A box contains CO(g), Cl_2 (g) and $COCl_2$ (g) in equilibrium at 1000 K. The removal of CO (g) will
   (a) decrease the concentration of $COCl_2$ (b) increase the concentration of Cl_2
   (c) increase the concentration of $COCl_2$
   (d) reduce the concentration of CO as well as Cl_2

8. An industrial fuel, 'water gas', which consists of a mixture of H_2 and CO can be made by passing steam over red-hot carbon. The reaction is $C(s)+H_2O(g) \rightleftharpoons CO(g)+H_2(g), \Delta H=+131\ kJ$ The yield of CO and H_2 at equilibrium would be shifted to the product side by
(a) raising the relative pressure of the steam
(b) adding hot carbon
(c) raising the temperature
(d) reducing the volume of the system

9. For the equilibrium, $2SO_2(g)+O_2(g) \rightleftharpoons 2SO_3(g), \Delta H=-198\ kJ,$
the equilibrium concentration of SO_3 will be affected by
(a) doubling the volume of the reaction vessel
(b) increasing the temperature at constant volume
(c) adding more oxygen to the reaction vessel
(d) adding helium to the reaction vessel at constant volume

10. The following reaction attains equilibrium at high temperature.
$N_2(g)+2H_2O(g)+heat \rightleftharpoons 2NO(g)+2H_2(g)$The yield of NO is affected by
(a) increasing the nitrogen concentration
(b) decreasing the hydrogen concentration
(c) compressing the reaction mixture
(d) none of these

11. $N_2(g)+3H_2(g) \underset{500^0C}{\overset{Catalyst}{\rightleftharpoons}} 2NH_3+heat$ In this reaction, the direction of equilibrium will be shifted to the right by
(a) increasing the concentration of nitrogen
(b) compressing the reaction mixture
(c) removing the catalyst
(d) decreasing the concentration of ammonia

12. The dissociation of ammonium carbamate may be represented by the equation $NH_4CO_2NH_2(s) \rightleftharpoons 2NH_3(g)+CO_2(g)$
ΔH^0 for the forward reaction is negative. The equilibrium will shift from right to left if there is
(a) a decrease in pressure
(b) an increase in temperature
(c) an increase in the concentration of ammonia
(d) an increase in the concentration of carbon dioxide

Level – 3

CHEMICAL AND IONIC EQUILIBRIUM

FILL IN THE BLANKS

1. The conjugate base of HSO_4^- in aqueous solutions is ....

2. An element which can exist as a positive ion in acidic solution and also as a negative ion in basic solution is said to be ....

3. Silver chloride is sparingly soluble in water because its lattice energy is greater than .... energy.

4. For a given reversible reaction at a fixed temperature, equilibrium constant K_p and K_c are related by ....

5. A ten-fold increase in pressure on the reaction, $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$ at equilibrium, results in .... in K_p.

6. In the reaction $I^- + I_2 \longrightarrow I_3^-$, the Lewis acid is ....

7. $(CH_3OH_2)^+$ is .... acidic than $(CH_3NH_3^+)$.

8. For a gaseous reaction $2B \longrightarrow A$, the equilibrium constant K_p is.............. to/than K_c.

TRUE /FALSE

9. Aluminium chloride ($AlCl_3$) is a Lewis acid because it can donate electrons.

10. When a liquid and its vapour are at equilibrium and the pressure is suddenly decreased, cooling occurs.

11. If equilibrium constant for the reaction, $A_2 + B_2 \rightleftharpoons 2AB$, is K, then for the backward reaction $AB \rightleftharpoons \frac{1}{2}A_2 + \frac{1}{2}B_2$, the equilibrium constant is $\frac{1}{K}$.

12. Solubility of sodium hydroxide increases with increase in temperature.

13. The following species are in increasing order of their acidic property: ZnO, Na_2O_2, P_2O_5, MgO

14. Catalyst makes a reaction more exothermic.

15. The rate of an exothermic reaction increases with increasing temperature.

Only one option is correct:

16. Pure ammonia is placed in a vessel at a temperature where its dissociation constant (α) is appreciable. At equilibrium:
(a) K_p does not change significantly with pressure.
(b) α does not change with pressure
(c) concentration of NH_3 does not change with pressure.
(d) concentration of hydrogen is less than that of nitrogen

17. A certain buffer solution contains equal concentration of X^- and HX. The K_b for X^- is 10^{-10}. Then pH of the buffer is:
(a) 4 (b) 7 (c) 10 (d) 14

18. A certain weak acid has a dissociation constant of 1.0×10^{-4}. The equilibrium constant for its reaction with a strong base is:
(a) 1.0×10^{-4} (b) 1.0×10^{-10} (c) 1.0×10^{10} (d) 1.0×10^{14}

19. An example of a reversible reaction is:
(a) $Pb(NO_3)_2$ (*aq*) + 2NaI (*aq*) = PbI_2(s) + $2NaNO_3$(*aq*)
(b) $AgNO_3$ (*aq*) + HCl (aq) =AgCl (s) + HNO_3 (*aq*)
(c) 2Na(s) + H_2O(*l*) = 2NaOH (*aq*) + H_2(g)
(d) KNO_3 (*aq*) + NaCl (*aq*) = KCl (*aq*) + $NaNO_3$ (*aq*)

20. The best indicator for detection of end point in titration of a weak acid and a strong base is:
(a) methyl orange (3 to 4) (b) methyl red (5 to 6)
(c) bromothymol blue (6 to 7.5) (d) phenolphathalein (8 to 9.6)

21. The conjugate acid of NH_2^- is:
(a) NH_3 (b) NH_2OH (c) NH_4^+ (d) N_2H_4

22. The compound that is not a Lewis acid is:
(a) BF_3 (b) $AlCl_3$ (c) $BeCl_2$ (d) $SnCl_4$

23. The pK_a of acetyl salicylic acid (aspirin) is 3.5. The pH of gastric juice in human stomach is about 2-3 and the pH in the small intestine is about 8. Aspirin will be:
(a) unionized in the small intestine and in the stomach
(b) completely ionized in the small intestine and in the stomach
(c) ionized in the stomach and almost unionized in the small intestine.
(d) ionized in the small intestine and almost unionized in the stomach

24. When equal volumes of the following solutions are mixed, precipitation of AgCl $\left(K_{sp} = 1.8 \times 10^{-10}\right)$ will occur only with:
(a) 10^{-4} M (Ag^+) and 10^{-4}M (Cl^-) (b) 10^{-5} M (Ag^+) and 10^{-5}M (Cl^-)
(c) 10^{-6} M (Ag^+) and 10^{-6}M (Cl^-) (d) 10^{-10} M (Ag^+) and 10^{-10}M (Cl^-)

25. Which of the following is the strongest acid?
(a) ClO_3 (OH) (b) ClO_2 (OH) (c) $SO(OH)_2$ (d) $SO_2(OH)_2$

26. Amongst the following hydroxides, the one which has the lowest value of K_{sp} at ordinary temperature (about 25^0C) is
(a) $Mg(OH)_2$ (b) $Ca(OH)_2$ (c) $Ba(OH)_2$ (d) $Be(OH)_2$

27. which of the following solutions will have pH close to 1.0?
(a) 100 mL of (M/10) HCl + 100 mL of (M/10) NaOH
(b) 55 mL of (M/10)HCl + 45 mL of (M/10) NaOH
(c) 10 mL of (M/10) HCl + 90 mL of (M/10) NaOH
(d) 75 mL of (M/5) HCl + 25 mL of (M/5) NaOH

28. One mole of N_2O_4 (g) at 300 K is kept in a closed container under one atmosphere. It is heated to 600 K when 20% by mass of N_2O_4(g) decomposes to NO_2 (g). The resultant pressure is:
(a) 1.2 atm (b) 2.4 atm (c) 2.0 atm (d) 1.0 atm

29. The pH of 0.1 M solution of the following salts increases in the order:
(a) NaCl < NH_4Cl < NaCH < HCl (b) HCl < NH_4Cl < NaCl < NaCN
(c) NaCN < NH_4Cl < NaCl < HCl (d) HCl < NaCl < NaCN < NH_4Cl

30. For the chemical reaction $3X(g) + Y(g) \rightleftharpoons X_3Y(g)$ the amount of X_3Y at equilibrium is affected by:
(a) temperature and pressure (b) temperature only
(c) pressure only (d) temperature pressure and catalyst

31. For the reversible reaction, $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$
at 500^0C, the value of K_p is 1.44×10^{-5} when partial pressure is measured in atmosphere. The corresponding value of K_c with concentration in mol/L is:
(a) $\frac{1.44 \times 10^{-5}}{(0.082 \times 500)^{-2}}$ (b) $\frac{1.44 \times 10^{-5}}{(8.314 \times 773)^{-2}}$
(c) $\frac{1.44 \times 10^{-5}}{(0.082 \times 773)^{2}}$ (d) $\frac{1.44 \times 10^{-5}}{(0.082 \times 773)^{-2}}$

32. At constant temperature, the equilibrium constant (K_p) for the decomposition reaction, $N_2O_4 \rightleftharpoons 2NO_2$, is expressed by
$K_p = \frac{(4x^2P)}{(1-x^2)}$, where P = Pressure, x = extent of decomposition. Which one of the following statement is true?
(a) K_p increases with increase of P (b) K_p increases with increase of x
(c) K_p increases with decrease of x
(d) K_p remains constant with change in P and x

33. For a sparingly soluble salt A_pB_q, the relationship of its solubility product (L_s) with its solubility (s) is:

(a) $L_s = S^{p+q}.P^p.q^q$ (b) $L_s = S^{p+q}.P^q.q^p$

(c) $L_s = S^{pq}.P^p.q^q$ (d) $L_s = S^{pq}.(P.q)^{(p+q)}$

34. Consider the following equilibrium in a closed container

$$N_2O_4(g) \rightleftharpoons 2NO_2(g)$$

At a fixed temperature, the volume of the reaction container is halved. For this change, which of the following statements hold true regarding the equilibrium constant (K_p) and degree of dissociation (α)?

(a) Neither K_p nor α changes (b) Both K_p and α change

(c) K_p changes but α does not change (d) K_p does not change but α changes

35. Which of the following acids has the smallest dissociation constant?

(a) $CH_3CHFCOOH$ (b) FCH_2CH_2COOH

(c) $BrCH_2CH_2COOH$ (d) $CH_3CHBrCOOH$

36. A solution which is 10^{-3} M each in Mn^{2+}, Fe^{2+}, Zn^{2+} and Hg^{2+} is treated with 10^{-16} M sulphide ion. If K_{sp} of MnS, FeS, ZnS and HgS are 10^{-15}, 10^{-23}, 10^{-20} and 10^{-54} respectively, which one will precipitate first.

(a) FeS (b) MgS (c) HgS (d) ZnS

37. HX is a weak acid ($K_a = 10^{-5}$). It forms a salt NaX (0.1M) on reacting with caustic soda. The degree of hydrolysis of NaX is:

(a) 0.01% (b) 0.0001% (c) 0.1% (d) 0.5%

38. 0.1 mole of CH_3NH_2 ($K_b = 5 \times 10^{-4}$) is mixed with 0.08 mole of HCl and diluted to one litre. What will be the H^+ concentration in the solution?

(a) 8×10^{-2} M (b) 8×10^{-11} M (c) 1.6×10^{-11} M (d) 8×10^{-5} M

39. $Ag^+ + NH_3 \rightleftharpoons [Ag(NH_3)]^+;\ k_1 = 3.5 \times 10^{-3}$

$[Ag(NH_3)]^+ + NH_3 \rightleftharpoons [Ag(NH_3)_2]^+;\ k_2 = 1.7 \times 10^{-3}$

then the formation constant of $[Ag(NH_3)_2]^+$ is:

(a) 6.08×10^{-6} (b) 6.08×10^{6} (c) 6.08×10^{-9} (d) none of these

More than one options are correct:

40. For the gas phase reaction.

$C_2H_4 + H_2 \rightleftharpoons C_2H_6$ $(\Delta H = -32.7\text{kcal})$

Carried out in a vessel, the equilibrium concentration of C_2H_4 can be increased by:

(a) increasing the temperature (b) decreasing the pressure

(c) removing some H_2 (d) adding some C_2H_6

41. When $NaNO_3$ is heated in a closed vessel, oxygen is liberated and $NaNO_2$ is left behind. At equilibrium:
(a) addition of $NaNO_2$ favours reverse reaction
(b) addition of $NaNO_3$ favours forward reaction
(c) increasing temperature favours forward reaction
(d) increasing pressure favours reverse reaction

42. The equilibrium $SO_2Cl_2(g) \rightleftharpoons SO_2(g) + Cl_2(g)$ is attained at 25°C in a closed container and an inert gas, helium is introduced. Which of the following statements are correct?
(a) Concentration of SO_2, Cl_2 and SO_2Cl_2 change
(b) More chlorine is formed
(c) concentration of SO_2 is reduced
(d) All are incorrect.

43. For the reaction; $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$
The forward reaction at constant temperature is favoured by:
(a) introducing an inert gas at constant volume
(b) introducing chlorine gas at constant volume
(c) introducing an inert gas at constant pressure
(d) increasing the volume of the container
(e) introducing PCl_5 at constant volume

44. For the reaction; $CO(g) + H_2O(g) \rightleftharpoons CO_2(g) + H_2(g)$,
at a given temperature, the equilibrium amount of $CO_2(g)$ can be increased by:
(a) adding a suitable catalyst (b) adding an inert gas
(c) decreasing the volume of the container
(d) increasing the amount of CO(g)

45. Which of the following statement (s) is (are) correct?
(a) The pH of 1.0×10^{-8} M solution of HCl is 8
(b) The conjugate base of $H_2PO_4^-$ is HPO_4^{2-}
(c) Autoprotolysis constant of water increases with temperature
(d) When a solution of a weak monoprotic acid is treated against a strong base, at half-neutralisation point $pH = \left(\frac{1}{2}\right)pK_a$

46. A buffer solution can be prepared from a mixture of:
(a) sodium acetate and acetic acid in water
(b) sodium acetate and HCl in water
(c) ammonia and ammonium chloride in water
(d) ammonia and sodium hydroxide in water

47. When two reactants, A and B are mixed to give products, C and D, the reaction quotient, (Q) at the initial stages of the reaction:
(a) is zero (b) decreases with time
(c) is independent of time (d) increases with time

Level - 1
Chemical Equilibrium
Answer key

Q.	Ans.	Q.	Ans.	Q.	Ans.	Q.	Ans.
1.	B	11.	C	21.	C	31.	C
2.	C	12.	B	22.	C	32.	C
3.	D	13.	D	23.	C	33.	A
4.	A	14.	B	24.	A	34.	A
5.	B	15.	C	25.	A	35.	D
6.	A	16.	C	26.	A		
7.	D	17.	D	27.	D		
8.	D	18.	D	28.	C		
9.	A	19.	D	29.	A		
10.	A	20.	C	30.	B		

SOLUTION

1. $K_p = K_c(RT)^{\Delta n}$ or $K_c = K_p(RT)^{-\Delta n}$

2. $\Delta n_g = 2 - 3 = -1$ $\quad\therefore\quad$ $K_p = K_c(RT)^{-1} = K_c/RT$

3. $\Delta n_g = 1 - \left(1\frac{1}{2}\right) = -\frac{1}{2}$ $\quad\therefore\quad$ $K_p = K_c(RT)^{-1/2}$ or $K_p/K_c = (RT)^{-1/2}$

4. $K_p = K_c$ when $\Delta n_g = 0$.

5. K = Product of eqm. Constants of step reactions.

6. Reaction (b) is double of (a) and reverse of (a).

Hence $K_2 = \frac{1}{K_1^2}$ or $K_1^2 = \frac{1}{K_2}$.

7. As the reaction is reversed and divided by 2, new eqm. Const. = $\sqrt{\frac{1}{64}} = \frac{1}{8}$.

8. Apply law of chemical equilibrium

9. $2SO_2 + O_2 \rightleftharpoons 2SO_3$

Initial 2 moles 1 mole 0
At eqm. (2 - 2x) (1 – x) 2x
= 2(1 – x)
Molar 2(1 - x)/V (1 – x)/V 2x/V conc.

$$K = \frac{(2x/V)^2}{\left[\frac{2(1-x)}{V}\right]^2 \frac{(1-x)}{V}} = \frac{x^2V}{(1-x)^3}$$

10. $\underset{1}{A} \rightleftharpoons \underset{0}{2B}$ $P_A = \frac{1-\alpha}{1+\alpha}P, \; P_B = \frac{2\alpha}{1+\alpha}P$

$1 - \alpha$ 2α
Total = $1 + \alpha$

$$K_p = \frac{P_B^2}{P_A} = \frac{\left(\frac{2\alpha}{1+\alpha}.P\right)^2}{\left(\frac{1-\alpha}{1+\alpha}P\right)} = \frac{4\alpha^2 P}{1-\alpha^2}.$$

11. $K = \frac{\left[Cu^{2+}\right]\left[Ag(s)\right]^2}{\left[Cu(s)\right]\left[Ag^+\right]^2} = \frac{\left[Cu^{2+}\right]}{\left[Ag^+\right]^2}$ as $\left[\text{solid}\right] = 1$

12. The amount of A reacted is double the amount of B reacted.

13. K depends upon units of concentrations when $n_p \neq n_r$

14. On adding more PCl_5, equilibrium shifts forward.

15. Pressure has no effect when $n_p = n_r$

16. Low pressure favours forward reaction when $n_p > n_r$

17. (d) By Le-chatelier principle.

18. Reaction is exothermic with $n_p < n_r$

19. Eqm. Const. Of a reaction depends only on temperature.

20. Eqm. Const. does not depend upon concentrations.

21. Vapours and liquid are at the same temperature.

22. $K = k_{f/k_b} = k_1/k_2$.

23. $K = [MX_3]^2/[MX_2]^2[X_2]$ is for $2\ MX_2 + X_2 \rightleftharpoons 2\ MX_3$.

24. Reaction (2) is inverse of (1) and half of (1).

Hence $K_2 = \sqrt{\frac{1}{K_1}}$ or $K_1 = \left(\frac{1}{K_2}\right)^2$.

25. Greater the value of K, more it goes towards completion.

26. $n_p < n_r$ and reaction is endothermic. Hence high pressure and high temp. will favour forward reaction.

27. The first two are the step reactions of the required reaction.

28. Reaction (ii) is inverse and double of (i). Hence $K_2 = 1/K_1^2$.

29. $K_p = \frac{P_C}{P_A^2 \times P_B} = \frac{1}{p^2} = atm^{-2}$.

30. $Fe^{3+} + SCN^- \rightarrow FeSCN^{2+}$ (Red colour).

31. $K = \frac{[NO_2]^2}{N_2O_4} = \frac{(2\times10^{-3}/2)^2}{(0.2/2)} = \frac{10^{-6}}{10^{-1}} = 10^{-5}$.

32.

	A	+	2B	$\rightleftharpoons$	2C	+	D
Initial moles	1.1		2.2				
Moles at eqm.	1.0		2.0		0.2		0.1

$$K = \frac{(0.2/V)^2(0.1/V)}{(1/V)(2/V)^2} = 0.001$$

33.

	A	+	2B	$\rightleftharpoons$	C
Initial moles	1		0.5		
Moles at eqm.	0.9		0.3		0.1
Molar concs.	0.3		0.1		0.1/3

$$K = \frac{0.1/3}{0.3\times(0.1)^2} = 11.11$$

34.

	H_2	+	I_2	$\rightleftharpoons$	2 HI
Initial	1 mole		2 moles		
At. eqm.	0.2 mole		2-0.8		2×0.8

= 1.2 mole = 1.6 mole

(0.8 mole of H_2 have reacted)

35. (D) $P_{N_2O_4} = \frac{1-\alpha}{1+\alpha}P$, $P_{NO_2} = \frac{2\alpha}{1+\alpha}P$, $K_p = \frac{\left(\frac{2\alpha}{1+\alpha}P\right)^2}{\left(\frac{1-\alpha}{1+\alpha}P\right)} = \frac{4\alpha^2 P}{1-\alpha^2}$

Level – 2

Q.	Ans.	Q.	Ans.	Q.	Ans.
1.	a, b, c	2.	a, c, d	3.	a, b, c, d
4.	a, b	5.	b, d	6.	a, b, c, d
7.	a, b	8.	a, c	9.	a, b, c
10.	a, b, c	11.	a, b, d	12,	b, c, d

Level – 3

FILL IN THE BLANKS

1. $\underset{\text{acid}}{HSO_4^-} \rightleftharpoons H^+ + \underset{\text{conjugate base}}{SO_4^{2-}}$;

2. amphoteric

3. hydration, solvation

4. $K_p = K_c\,(RT)^{\Delta n}$
where, Δn = No. of moles of gaseous products – No. of moles of gaseous reactants
R = Gas constant
T = Absolute temperature

5. no change for reversible reaction

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$

$$K_p = \frac{(2x^2)(a+b-2x)^2}{(a-x)(b-3x)^2 \times P^2},$$

where, *a* and *b* are the moles of N_2 and H_2 at t = 0.*x* is the change in moles of N_2 into NH_3 and P is total pressure at equilibrium. On increasing in pressure on the reaction in equilibrium results in **no change** in K_p.

6. I_2

7. Conjugate base of $(CH_3OH_2)^+$ i.e., CH_3OH is less basic than the conjugate base of $(CH_3NH_3)^+$ i.e., CH_3NH_2.

8. $K_p = K_c (RT)^{\Delta n_g}$
for given reaction, $\Delta n_g = 1 - 2 = -1$
$\therefore \quad K_p = K_c(RT)^{-1} \quad$ or $\quad K_p < K_c$

TRUE /FALSE

9. Lewis acids are the species which can accept lone pair of electron.

10. For reaction, $AB \rightleftharpoons \frac{1}{2}A_2 + \frac{1}{2}B_2$,
equilibrium constant = $1/\sqrt{K}$

11. **False:** for, $A_2 + B_2 \rightleftharpoons 2AB$

$$K = \frac{[AB]^2}{[A_2][B_2]}$$

For, $AB \rightleftharpoons \frac{1}{2}A_2 + \frac{1}{2}B_2$

$$K' = \frac{[A_2]^{1/2}[B_2]^{1/2}}{[AB]}$$

$\therefore \quad K' = \sqrt{\frac{1}{K}}$

12. **False:** Sodium hydroxide is a strong base. It is completely ionized and its solubility in water is an exothermic reaction.

13. **False:** $Na_2O_2 < MgO < ZnO < P_2O_5$.

14. **False:** Catalyst does not make a reaction more exothermic.

15. **False:** The rate of an exothermic reaction decreases with increasing temperature.

(*Only one option is correct:)*

16. At equilibrium, K_p does not change significantly with pressure.

17. $K_a \times K_b = 10^{-14}$
Thus, $\quad K_a \times 10^{-10} = 10^{-14} \quad$ or $\quad K_a = 10^{-4}$

Now, $$\text{pH} = -\log K_a + \log\frac{[\text{salt}]}{[\text{acid}]} = -\log 10^{-4} + \log\frac{1.0}{1.0} = 4$$

18. $$\underset{\text{weak}}{HA} + \underset{\text{strong}}{BOH} \rightleftharpoons BA + H_2O$$

$$\therefore \quad HA + B^+OH^- \rightleftharpoons B^+ + A^- + H_2O \quad \text{or} \quad HA + OH^- \rightleftharpoons A^- + H_2O$$

$$\therefore \quad K = \frac{\left[A^-\right]}{\left[HA\right]\left[OH^-\right]} \qquad \ldots(1)$$

Also for weak acid, $HA : HA \rightleftharpoons H^+ + A^-$

$$K_a = \frac{\left[H^+\right]\left[A^-\right]}{[HA]} \qquad \ldots(2)$$

By equation (1) and (2)

$$\frac{K_a}{K} = K_w \quad \text{or} \quad \frac{K_a}{K_w} = \frac{1\times10^{-4}}{1\times10^{-14}}, K = 1\times10^{10}$$

19. The reaction, KNO_3 (*aq*) + NaCl (*aq*) = KCl (*aq*) + $NaNO_3$ (*aq*) is an ion exchange reaction. Hence it is a reversible reaction.

20. Phenolphthalein is a good indicator if the base is strong, because strong base immediately changes the pH at end point.

21. $$NH_2^- + H^+ \longrightarrow \underset{\text{conjugate acid}}{NH_3}$$

22. $AlCl_3$ acts as Lewis base, because it is electron deficient (Al atom in it has 6 electrons) and thus capable of accepting electron pair.

23. Aspirin, being a weak acid is unionized in acid medium (common ion effect) and completely ionized in alkaline medium.

24. $$AgCl \rightleftharpoons \left[Ag^+\right] + \left[Cl^-\right] = \left(\frac{10^{-4}\times V}{2V}\right)\left(\frac{10^{-4}\times V}{2V}\right)^2 = 2.5\times10^{-9}$$

This value is greater than $K_{sp} = 1.8 \times 10^{-10}$

25. Greater is the oxidation number of the central atom in oxy acid, more is its acidic nature.

26. The solubility of these hydroxides follows the order:
$Ba(OH)_2 > Ca(OH)_2 > Mg(OH)_2 > Be(OH)_2$

27. 75 mL of $\frac{M}{5}$ HCl + 25 mL of $\frac{M}{5}$ NaOH

Meq. of HCl = 15 (∵ Mol. wt. and Eq. wt. of HCl or NaOH are same)
Meq. of NaOH = 5
Hence, in solution 10 meq. of HCl are remained in 100 mL solution.

So, conc. of HCl in mixture = $\frac{10}{100}M = \frac{M}{10}$

In $\frac{M}{10}$ HCl, $[H^+] = 10^{-1}M$

$$pH = -\log[H^+] = -\log 10^{-1} = 1$$

28. $N_2O_4(g) \rightleftharpoons 2NO_2(g)$

$\frac{100}{92}$ mole	0	At t = 0
$\frac{80}{92}$ mole	$\frac{20}{46}$ mole	at equilibrium

(∵ At equilibrium 20% NO_2 is formed by mass, ∴ 80% N_2O_4 is remained by mass)

At t = 0 (initially)

$$P_0V = n_0 RT_0$$

∴ $1 \times V = \frac{100}{92} \times 0.0821 \times 300$ or $V = 26.77L$

At equilibrium

$$P_2V = n_2RT_2$$

$$P_2 \times 26.77 = \left[\frac{80}{92} + \frac{20}{46}\right] \times 0.0821 \times 600$$

or $P_2 \times 26.77 = 1.3 \times 0.0821 \times 600$

∴ $P_2 = 2.4$ atm

Hence, the resulting pressure = 2.4 atm

29. In these HCl is stronger acid, aqueous NH_4Cl solution is slightly acidic (pH is lowest)

$NH_4Cl + H_2O \rightleftharpoons NH_4OH + HCl$, $[H^+] > [OH^-]$

Aqueous NaCN solution is basic

$NaCN + H_2O \rightleftharpoons NaOH + HCN$, $[OH^-] > [H^+]$

Aqueous NaCl solution is neutral.
Hence, increasing order of pH HCl < NH_4Cl < NaCl < NaCN

30. Equilibrium is affected by temperature and pressure due to change in heat as well as change in volume of substances.

31. $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$

Δn = No. of gaseous moles of right side – No. of gaseous moles of left side = 2 – 4 = -2

As we know that, $K_p = K_c (RT)^{\Delta n}$

$$1.44\times10^{-5} = K_c \times (0.0821 \times 773)^{-2}$$

$$\therefore \quad K_c = \frac{1.44\times10^{-5}}{(0.0821\times773)^{-2}}\left(\text{mol}/\text{L}^{-2}\right)$$

32. K_p is not based upon pressure and concentration.

33. $A_pB_q \rightleftharpoons pA^+ + qB^-$

Solubility S, pS, qS (on 100% ionization)

$$K_{sp} \text{ of } A_pB_q = [A^+]^p \times [B^-]^q = (pS)^p \times (qS)^q = S^{p+q}\left(p^p.q^q\right)$$

34. For equilibrium $N_2O_4(s) \rightleftharpoons 2NO_2(g)$

At equilibrium (1 – α) mole 2α mole

Total moles = 1 – α + 2α = 1 + α

If P is total pressure at equilibrium therefore

$$P_{N_2O_4} = \frac{1-\alpha}{1+\alpha}.P \quad \text{and} \quad P_{NO_2} = \frac{2\alpha}{1-\alpha}.P$$

$$K_p = \frac{\left(P_{NO_2}\right)^2}{P_{N_2O_2}} = \frac{4\alpha^2 \times P}{(1-\alpha)(1+\alpha)}$$

If volume is halved, therefore pressure is doubled but the value of K_p is not effected with pressure. Thus at higher P K_p will be higher, but it is constant so for maintaining the constant value of K_p, α will be lowered. Hence K_p does not changed, but α changes.

35. Acidic strength ∝ dissociation constant of acid. In given acids order of acidic strength:

$CH_3CHFCOOH > CH_3CHBrCOOH > FCH_2CH_2COOH > BrCH_2CH_2COOH$

Hence, in these smallest dissociation constant will be for

$BrCH_2—CH_2—COOH$.

36. On the basis of precipitation concept an electrolyte will be precipitated firstly whose ionic product is exceeded to its solubility product. In similar ionic conc. of cations/an electrolyte is precipitated firstly for which K_{sp} is lower. In these electrolytes MnS, ZnS, and HgS, HgS is precipitate firstly.

37. $NaX + H_2O \rightleftharpoons NaOH + HX$

In it HX is weak acid, so NaX is a salt of weak acid and strong base.

∴ Hydrolysis constant of NaX

$$K_h = \frac{K_w}{K_a} = \frac{1\times10^{-14}}{10^{-5}} = 1\times10^{-9}$$

For this type of salt $K_h = \frac{h^2}{V} = ch^2$

h = degree of hydrolysis

$\therefore$ $1\times 10^{-9} = 0.1 \times h^2$ or $h^2 = \dfrac{1\times 10^{-9}}{0.1} = 1\times 10^{-8}$

$h = 1\times 10^{-4}$

$\therefore$ % of degree of hydrolysis of NaX salt $=1\times10^{-4} \times 100 = 1 \times 10^{-2} = 0.01$ %

38. CH_3NH_2 (base) on reaction with HCl (acid) to give a salt of weak base and strong acid as $CH_3NH_3^+Cl^{-1}$

$$CH_3NH_2 \quad + \quad HCl \longrightarrow CH_3NH_3^+Cl^-$$

At t = 0 0.1 mole 0.08 mole 0
After reaction (0.1-0.08) mole
=0.02 mole 0.08 mole

So, it acts as basic buffer solution due to presence of base and salt is solution of one litre

$$pOH = -\log_{10} K_b + \log_{10}\frac{[Salt]}{[Base]}$$

$$pOH = -\log_{10} K_b + \log_{10}\frac{[CH_3NH_3^+Cl^-]}{[CH_3NH_2]}$$

$$= -\log_{10} 5\times10^{-4} + \log_{10}\frac{[0.08]}{[0.02]}$$

$$= -\log_{10} 5 + 4\log_{10} 10 + \log_{10}\frac{[0.08]}{[0.02]}$$

$$= -0.699 + 4 + 0.602 = 3.903$$

$$\therefore \; pH = 14 - pOH = 14 - 3.903 = 10.097 = -\log_{10}[H^+]$$

$$10.097 = -\log_{10}[H^+]$$

$$\therefore \qquad [H^+] = 8.0\times10^{-11}$$

39. $(i)\,Ag^+ + NH_3 \rightleftharpoons [Ag(NH_3)]^+, k_1 = 3.5\times10^{-3}$

$(ii)\,[Ag(NH_3)]^+ + NH_3 \rightleftharpoons [Ag(NH_3)_2]^+, k_2 = 1.7\times10^{-3}$

on the basis of above reaction

$$k_1 = \frac{\left[Ag(NH_3)\right]^+}{\left[Ag^+\right]\left[NH_3\right]} \qquad \ldots(i)$$

$$k_2 = \frac{\left[Ag(NH_3)_2\right]^+}{\left[Ag(NH_3)\right]^+\left[NH_3\right]} \qquad \ldots(ii)$$

For the formation of $\left[Ag(NH_3)_2\right]^+$

$$Ag^+ + 2NH_3 \rightleftharpoons \left[Ag(NH_3)_2\right]^+$$

$$\text{formation constant}\,(K) = \frac{\left[Ag(NH_3)_2\right]^+}{\left[Ag^+\right]\left[NH_3\right]^2} \qquad \ldots(iii)$$

From eq. (i) and (ii)

$$K = k_1 \times k_2$$

$$= 3.5 \times 10^{-3} \times 1.7 \times 10^{-3}$$

$$= 5.95 \times 10^{-6} \approx 6.08 \times 10^{-6}$$

(*More than* *one options are correct:*)

40. According to Le-Chatelier's principle.

41. $NaNO_3(s) \rightleftharpoons NaNO_2(s) + \frac{1}{2}O_2(g) \qquad \Delta H = +ve$

Since reaction is endothermic, forward reaction is favoured by increase in temperature. $K_p = [pO_2]^{1/2}$.
Thus, addition of $NaNO_2$ or $NaNO_3$ does not cause any change in K_p.

42. No change takes place in a closed container at constant volume when an inert gas is added.

43. According to Le-chatelier's principle.

44. $CO(g) + H_2O(g) \rightleftharpoons CO_2(g) + H_2(g)$

$$K_c = \frac{[CO_2][H_2]}{[CO][H_2O]}$$

A catalyst simply helps in attaining the equilibrium earlier. Addition of inert gas has no effect on a reaction because in it $\Delta n = 0$. This equilibrium is not based upon volume because in it $\Delta n = 0$. On increasing the amount of CO, K_c will be decreased but it is constant at constant temperature, so for maintaining the constant value of K_c, the amount of CO_2 increases.

45. pH of 1×10^{-8} M is below to 7

$$H_2PO_4^- + H_2O \rightleftharpoons \underset{\text{conjugate base of } H_2PO_4^- \text{ acid}}{HPO_4^{2-}} + H_3O^+$$

$$H_2O + H_2O \rightleftharpoons OH^- + H_3O^+$$

K (Auto protolysis constant of water i.e,. with ionic product of water) increases with temperature.

For half neutralization of a weak acid by a weak base

$$pH = pK_a + \log\frac{[salt]}{[acid]}$$

$$[salt] = [Acid] \qquad \therefore pH = pK_a$$

46. Because a buffer solution is prepared by mixing a weak acid/base with salt of its conjugate base/acid.

47. Reaction quotient = $\frac{[C][D]}{[A][B]}$

Initial stages (C) = 0 or [D] = 0

So, the value of quotient = $\frac{0}{[A][B]}$ = 0 and increases with time.

SET Self Evaluation Test - 8

1. One mole of SO_3 was placed in a litre reaction vessel at a certain temperature. The following equilibrium was established $2SO_3 \rightleftharpoons 2SO_2 + O_2$

At equilibrium 0.6 moles of SO_2 were formed. The equilibrium constant of the reaction will be **[MP PMT 1991]**

(a) 0.36 (b) 0.45

(c) 0.54 (d) 0.675

2. For the following homogeneous gas reaction $4NH_3 + 5O_2 \rightleftharpoons 4NO + 6H_2O$, the equilibrium constant K_c has the dimension of **[CPMT 1990; MP PET/PMT 1998]**

(a) $Conc^{+10}$ (b) $Conc^{+1}$

(c) $Conc^{-1}$ (d) It is dimensionless

3. Consider the imaginary equilibrium

$4A + 5B \rightleftharpoons 4X + 6Y$

The equilibrium constant K_c has the unit **[RPMT 2000]**

(a) Mole^2 *litre*$^{-2}$ (b) *Litre* mole^{-1}

(c) Mole *litre*$^{-1}$ (d) *Litre*^{2} mole^{-2}

4. For the reaction $CO(g) + 2H_2(g) \rightleftharpoons CH_3OH(g)$, true condition is

(a) $K_p = K_c$ (b) $K_p > K_c$

(c) $K_p < K_c$ (d) $K_c = 0$ but $K_p \neq 0$

5. For the reaction $CO(g) + \frac{1}{2}O_2(g) \rightleftharpoons CO_2(g)$; $\frac{K_p}{K_c}$ is equivalent to **[MP PET/PMT 1998; AIEEE 2002]**

(a) 1 (b) RT

(c) $\frac{1}{\sqrt{RT}}$ (d) $(RT)^{1/2}$

6. $\underset{(g)}{2N_2O_5} \rightarrow \underset{(g)}{4NO_2} + \underset{(g)}{O_2}$ what is the ratio of the rate of decomposition of N_2O_5 to rate of formation of NO_2 **[DCE 2003]**

(a) $1:2$ (b) $2:1$

(c) $1:4$ (d) $4:1$

7. The reaction quotient (*Q*) for the reaction

$N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)}$

is given by $Q = \frac{[NH_3]^2}{[N_2][H_2]^3}$. The reaction will proceed from right to left is **[CBSE PMT 2003]**

(a) *Q* = 0 (b) *Q* = K_c

(c) *Q* < K_c (d) *Q* > K_c

Where K_c is the equilibrium constant

8. In the thermal dissociation of PCl_5, the partial pressure in the gaseous equilibrium mixture is 1.0 atmosphere when half of PCl_5 is found to dissociate. The equilibrium constant of the reaction (K_p) in atmosphere is **[JIPMER 2002]**

(a) 0.25 (b) 0.50

(c) 1.00 (d) 0.3

9. HI was heated in a closed tube at $440^o C$ till equilibrium is obtained. At this temperature 22% of HI was dissociated. The equilibrium constant for this dissociation will be

[MP PET 1988, 92; MNR 1987; UPSEAT 2000]

(a) 0.282 (b) 0.0796

(c) 0.0199 (d) 1.99

10. The following equilibrium exists in aqueous solution $CH_3COOH \rightleftharpoons CH_3COO^- + H^+$. If dilute HCl is added without a change in temperature, then the **[MNR 1987]**

(a) Concentration of CH_3COO^- will increase

(b) Concentration of CH_3COO^- will decrease

(c) Equilibrium constant will increase

(d) Equilibrium constant will decrease

11. Which of the following is not favourable for SO_3 formation

$$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g); \Delta H = -45.0\,kcal$$

[IIT 1984; MP PET 1997]

(a) High pressure

(b) High temperature

(c) Decreasing SO_3 concentration

(d) Increasing reactant concentration

12. $120gm$ of urea are present in $5\,litre$ solution, the active mass of urea is **[MP PMT 1994]**

(a) 0.2 (b) 0.06

(c) 0.4 (d) 0.08

13. For the system $2A(g)+B(g)\rightleftharpoons 3C(g)$, the expression for equilibrium constant *K* is **[NCERT 1973; DCE 1999]**

(a) $\frac{[2A]\times[B]}{[3C]}$ (b) $\frac{[A]^2\times[B]}{[C]^3}$

(c) $\frac{[3C]}{[2A]\times[B]}$ (d) $\frac{[C]^3}{[A]^2\times[B]}$

14. If concentration of reactants is increased by $'x'$, then K becomes **[AFMC 1997]**

(a) ln (K/x) (b) K/x

(c) $K+x$ (d) K

Answers and Solutions

(SET -8)

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1. (d) $\underset{(1-0.6)}{2SO_3}\rightleftharpoons\underset{(0.6)}{2SO_2}+\underset{(0.3)}{O_2}$

$$K_c=\frac{[SO_2]^2[O_2]}{[SO_3]}=\frac{0.6\times0.6\times0.3}{0.4\times0.4}=0.675.$$

2. (b) *K* has the units of $(\text{conc})^{\Delta n}$, where $\Delta n=10-9=+1$

3. (c) Unit of $K_c=$ (unit of concentration)$^{\Delta n}$

= $(mole\ litre^{-1})^{\Delta n}$

$\Delta n = 10 - 9 = 1$

$\therefore\ K_c=\ mol\ Litre^{-1}$.

4. (c) When $n_r>n_p$ then $K_p<K_c$

where n_r = no. of moles of reactant

n_p = no. of moles of product.

5. (c) For $CO+\frac{1}{2}O_2\rightleftharpoons CO_2$

$$K_p=K_c(RT)^{1-1\frac{1}{2}}=K_c(RT)^{-\frac{1}{2}};$$

$$\frac{K_p}{K_c}=\sqrt{\frac{1}{RT}}$$

6. (b) $2N_2O_5\rightarrow HNO_2+O_2$

Rate of decomposition of N_2O_5

$$=-\frac{1}{2}.\frac{K[N_2O_5]}{dt}$$

Rate of formation of $NO_2=\frac{1}{4}.\frac{d[NO_2]}{dt}$

$\therefore$ Ratio = 2 : 1

7. (d) If $Q>K_c$ reaction will proceed right to left to decrease concentration of product.

8. (d) $PCl_5\rightleftharpoons PCl_3+Cl_2$

Initial conc. 1 0 0

At equilibrium 0.5 0.5 0.5

$$K_p=\frac{Px^2}{(1-x^2)}=\frac{1\times0.5\times0.5}{[1-(0.5)^2]}=\frac{0.5\times0.5}{0.75}=\frac{1}{3}=0.3$$

9. (c) $2HI\rightleftharpoons H_2+I_2$

Initial conc. 2 *moles* 0 0

at equilibrium $\frac{22}{100}\times2$ 0.22 0.22

$=2-0.44=1.56$

$$K=\frac{[H_2][I_2]}{[HI]^2}=\frac{0.22\times0.22}{[1.56]^2}=0.0199.$$

10. (b) When adding *HCl* in CH_3COOH solution the concentration of H^+ is increased. So reaction is proceed in reverse direction and the concentration of CH_3COO^- is decreased.

11. (b) The reaction is exothermic so high temperature will favour backward reaction.

12. (c) Active mass $=\frac{moles}{litre}$

$$=\frac{\text{wt. in } gm/\text{molecular wt.}}{V\text{ in } litre}=\frac{120/60}{5}=\frac{2}{5}=.4$$

13. (d) $K=\frac{[C]^3}{[A]^2[B]}$.

14. (d) There is no effect of change in concentration on equilibrium constant.

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Ionic Equilibrium

OT Ordinary Thinking

Objective Questions

Electrical conductors, Arrhenius theory and Ostwald's dilution law

1. Which of the following is non-electrolyte **[CPMT 2001]**

(a) $NaCl$ (b) $CaCl_2$

(c) $C_{12}H_{22}O_{11}$ (d) CH_3COOH

2. Ammonium hydroxide is a **[CPMT 1977]**

(a) Strong electrolyte

(b) Weak electrolyte

(c) Both under different conditions

(d) Non-electrolyte

3. Ammonium hydroxide is a weak base because **[MP PET 2000]**

(a) It has low vapour pressure

(b) It is only slightly ionized

(c) It is not a hydroxide of any metal

(d) It has low density

4. Electrolytes when dissolved in water dissociate into their constituent ions. The degree of dissociation of an electrolyte increases with **[CPMT 1974]**

(a) Increasing concentration of the electrolyte

(b) Decreasing concentration of the electrolyte

(c) Decreasing temperature

(d) Presence of a substance yielding a common ion

5. An electrolyte **[MP PMT/PET 1988; CPMT 1974]**

(a) Gives complex ions in solution

(b) Dissolves in water to give ions

(c) Is ionized in the solid state

(d) Generates ions on passing electric current

6. A monoprotic acid in 1.00 *M* solution is 0.01% ionised. The dissociation constant of this acid is **[BVP 2003]**

(a) 1×10^{-8} (b) 1×10^{-4}

(c) 1×10^{-6} (d) 10^{-5}

7. Molten sodium chloride conducts electricity due to the presence of **[BHU 2001]**

(a) Free electrons

(b) Free ions

(c) Free molecules

(d) Atoms of sodium and chlorine

8. An example for a strong electrolyte is **[KCET 2002]**

(a) Urea (b) Ammonium hydroxide

(c) Sugar (d) Sodium acetate

9. Which one is strongest electrolyte in the following **[CPMT 1990]**

(a) $NaCl$ (b) CH_3COOH

(c) NH_4OH (d) $C_6H_{12}O_6$

10. The equivalent conductance at infinite dilution of a weak acid such as HF **[Pb. PMT 1998]**

(a) Can be determined by measurement of very dilute HF solution

(b) Can be determined by extrapolation of measurements on dilute solutions of HCl, HBr and HI

(c) Can best be determined from measurements on dilute solutions of NaF, $NaCl$ and HCl

(d) Is an undefined quantity

11. If α is the degree of ionization, C the concentration of a weak electrolyte and K_a the acid ionization constant, then the correct relationship between α, C and K_a is **[CET Pune 1998; Pb. PMT 1998; RPMT 2002]**

(a) $\alpha^2 = \sqrt{\frac{K_a}{C}}$ (b) $\alpha^2 = \sqrt{\frac{C}{K_a}}$

(c) $\alpha = \sqrt{\frac{K_a}{C}}$ (d) $\alpha = \sqrt{\frac{C}{K_a}}$

12. Theory of ionization was given by **[AMU 1983; DPMT 1985]**

(a) Rutherford (b) Graham

(c) Faraday (d) Arrhenius

13. An ionizing solvent has

(a) Low value of dielectric constant

(b) High value of dielectric constant

(c) A dielectric constant equal to 1

(d) Has a high melting point

14. The extent of ionization increases **[MNR 1982]**

(a) With the increase in concentration of solute

(b) On addition of excess water to solution

(c) On decreasing the temperature of solution

(d) On stirring the solution vigorously

15. Which is generally true about ionic compounds **[Pb. PMT 2002]**

(a) Have low boiling point

(b) Have low melting point

(c) Soluble in non polar solvents

(d) Conduct electricity in the fused state

16. At infinite dilution, the percentage ionisation for both strong and weak electrolytes is **[CPMT 1999]**

(a) 1% (b) 20%

(c) 50% (d) 100%

17. The degree of ionization of a compound depends on **[MNR 1980]**

(a) Size of solute molecules

(b) Nature of solute molecules

(c) Nature of vessel used

(d) Quantity of electricity passed

18. For a weak acid HA, Ostwald's dilution law is represented by the equation

(a) $K_a = \frac{\alpha c}{1-\alpha^2}$ (b) $K_a = \frac{\alpha^2 c}{1-\alpha}$

(c) $\alpha = \frac{K_a c}{1-c}$ (d) $K_a = \frac{\alpha^2 c}{1-\alpha^2}$

19. Acetic acid is a weak electrolyte because **[CPMT 1974]**

(a) Its molecular weight is high

(b) It is covalent compound

(c) It does not dissociate much or its ionization is very less

(d) It is highly unstable

20. In which of the following dissociation of NH_4OH will be minimum **[MP PET 2000]**

(a) $NaOH$ (b) H_2O

(c) NH_4Cl (d) $NaCl$

21. Vant hoff factor of $BaCl_2$ of conc. $0.01M$ is 1.98. Percentage dissociation of $BaCl_2$ on this conc. Will be **[Kerala CET 2005]**

(a) 49 (b) 69

(c) 89 (d) 98

(e) 100

22. In which of the following solutions, ions are present **[NCERT 1981]**

(a) Sucrose in water (b) Sulphur in CS_2

(c) Caesium nitrate in water (d) Ethanol in water

23. The following equilibrium exists inaqueous solution, $CH_3COOH \rightleftarrows CH_3COO^- + H^+$ if dil HCl is added, without change in temperature, the **[UPSEAT 2000, 02]**

(a) Concentration of CH_3COO^- will increase

(b) Concentration of CH_3COO^- will decrease

(c) The equilibrium constant will increase

(d) The equilibrium constant will decrease

24. Which will not affect the degree of ionisation **[MP PMT 1994]**

(a) Temperature (b) Concentration

(c) Type of solvent (d) Current

25. The addition of a polar solvent to a solid electrolyte results in **[NCERT 1973]**

(a) Polarization (b) Association

(c) Ionization (d) Electron transfer

26. The degree of dissociation of $0.1M\ HCN$ solution is 0.01%. Its ionisation constant would be **[RPMT 1999]**

(a) 10^{-3} (b) 10^{-5}

(c) 10^{-7} (d) 10^{-9}

27. The hydrogen ion concentration in weak acid of dissociation constant K_a and concentration C is nearly equal to **[CBSE PMT 1989; RPMT 2000]**

(a) $\sqrt{K_a / c}$ (b) c / K_a

(c) $K_a c$ (d) $\sqrt{K_a c}$

28. Degree of dissociation of $0.1N\ CH_3COOH$ is (Dissociation constant $= 1 \times 10^{-5}$) **[MP PET 1997]**

(a) 10^{-5} (b) 10^{-4}

(c) 10^{-3} (d) 10^{-2}

29. Which of the following substance is an electrolyte **[MADT Bihar 1980]**

(a) Chloroform

(b) Benzene

(c) Toluene

(d) Magnesium chloride

30. In weak electrolytic solution, degree of ionization

(a) Will be proportional to dilution

(b) Will be proportional to concentration of electrolyte

(c) Will be proportional to the square root of dilution

(d) Will be reciprocal to the dilution

31. 0.2 molar solution of formic acid is ionized 3.2%. Its ionization constant is **[MP PMT 1991]**

(a) 9.6×10^{-3} (b) 2.1×10^{-4}

(c) 1.25×10^{-6} (d) 4.8×10^{-5}

32. The best conductor of electricity is a 1.0 *M* solution of **[NCERT 1973]**

(a) Boric acid (b) Acetic acid

(c) Sulphuric acid (d) Phosphoric acid

33. The colour of an electrolyte solution depends on **[DPMT 1985]**

(a) The nature of the anion

(b) The nature of the cation

(c) The nature of both the ions

(d) The nature of the solvent

34. Ionisation depends upon **[CPMT 2004]**

(a) Pressure (b) Volume

(c) Dilution (d) None of these

35. The values of dissociation constants of some acids (at 25^0C) are as follows. Indicate which is the strongest acid in water **[MP PMT 1991]**

(a) 1.4×10^{-2} (b) 1.6×10^{-4}

(c) 4.4×10^{-10} (d) 4.3×10^{-7}

36. Concentration CN^- in $0.1M\ HCN$ is $[K_a = 4 \times 10^{-10}]$

[RPET 2000]

(a) $2.5 \times 10^{-6} M$ (b) $4.5 \times 10^{-6} M$

(c) $6.3 \times 10^{-6} M$ (d) $9.2 \times 10^{-6} M$

Acids and Bases

1. Which of the following is not a Lewis acid **[MP PET 2002]**

(a) CO (b) $SiCl_4$

(c) SO_3 (d) Zn^{2+}

2. Review the equilibrium and choose the correct statement $HClO_4 + H_2O \rightleftarrows H_3O^+ + ClO_4^-$ **[RPMT 2000]**

(a) $HClO_4$ is the conjugate acid of H_2O

(b) H_3O^+ is the conjugate base of H_2O

(c) H_2O is the conjugate acid of H_3O^+

(d) ClO_4^- is the conjugate base of $HClO_4$

3. A solution of $FeCl_3$ in water acts as acidic due to **[BVP 2003]**

(a) Hydrolysis of Fe^{3+} (b) Acidic impurities

(c) Dissociation (d) Ionisation

4. A white substance having alkaline nature in solution is **[BVP 2003]**

(a) $NaNO_3$ (b) NH_4Cl

(c) Na_2CO_3 (d) Fe_2O_3

5. Which of the following can act both as Bronsted acid and Bronsted base **[MP PET 1995; MP PET/PMT 1998]**

(a) Cl^- (b) HCO_3^-

(c) H_3O^+ (d) OH^-

6. Lewis acid **[MP PMT 1987]**

(a) Presence of *H* atom is necessary

(b) Is a electron pair donor

(c) Always a proton donor

(d) Is a electron pair acceptor

7. For two acids *A* and B, $pK_a = 1.2$, $pK_b = 2.8$ respectively in value, then which is true **[Bihar MEE 1998]**

(a) *A* and *B* both are equally acidic

(b) *A* is stronger than *B*

(c) *B* is stronger than *A*

(d) Neither *A* nor *B* is strong

(e) None of these

8. Aq. solution of sodium cyanide is **[BHU 1981]**

(a) Acidic (b) Amphoteric

(c) Basic (d) Netural

9. Which of the following is the strongest conjugate base

[MADT Bihar 1983; CBSE PMT 1999; KCET (Med.) 2001]

(a) Cl^- (b) CH_3COO^-

(c) SO_4^{--} (d) NO_2^-

10. $NaOH$ is a strong base because **[AIIMS 2001]**

(a) It gives OH^- ion (b) It can be oxidised

(c) It can be easily ionised (d) Both (a) and (c)

11. Which one of the following can be classified as a Bronsted base **[KCET 2001]**

(a) NO_3^- (b) H_3O^+

(c) NH_4^+ (d) CH_3COOH

12. Which one of the following substance has the highest proton affinity **[AIEEE 2003]**

(a) H_2O (b) H_2S

(c) NH_3 (d) PH_3

13. Which of the following is the strongest Lewis acid **[EAMCET 1998]**

(a) BI_3 (b) BBr_3

(c) BCl_3 (d BF_3

14. An aqueous solution of ammonia consists of **[MP PET 2001]**

(a) H^+ (b) OH^-

(c) NH_4^+ (d) NH_4^+ and OH^-

15. Which of the following is not a Lewis acid **[CBSE PMT 1996]**

(a) BF_3 (b) $FeCl_3$

(c) SiF_4 (d) C_2H_4

16. The conjugate base of NH_2^- is **[EAMCET 1998]**

(a) NH_3 (b) NH^{2-}

(c) NH_4^+ (d) N_3^-

17. The strength of an acid depends on its tendency to **[MP PET 1996]**

(a) Accept protons (b) Donate protons

(c) Accept electrons (d) Donate electrons

18. Which is not a electrophile **[RPET 1999]**

(a) $AlCl_3$ (b) BF_3

(c) $(CH_3)_3C^+$ (d) NH_3

19. Ammonia gas dissolves in water to give NH_4OH. In this reaction water acts as **[CPMT 1990; MP PMT 1990]**

(a) An acid (b) A base

(c) A salt (d) A conjugate base

20. In the equilibrium

$CH_3COOH + HF \rightleftarrows CH_3COOH_2^+ + F^-$ **[BHU 1987]**

(a) F^- is the conjugate acid of CH_3COOH

(b) F^- is the conjugate base of HF

(c) CH_3COOH is the conjugate acid of $CH_3COOH_2^+$

(d) $CH_3COOH_2^+$ is the conjugate base of CH_3COOH

21. The compound that is not a Lewis acid is **[IIT 1985]**

(a) BF_3 (b) $AlCl_3$

(c) $BeCl_2$ (d) NH_3

22. Which of the following dissolves in water to give a neutral solution **[Bihar MADT 1980]**

(a) $(NH_4)_2SO_4$ (b) $Ba(NO_3)_2$

(c) $CrCl_3$ (d) $CuSO_4$

23. Which of the following is the strongest acid **[AMU 1982]**

(a) H_3PO_4 (b) H_2SO_4

(c) HNO_2 (d) CH_3COOH

24. An example of a Lewis acid is

[MADT Bihar 1982; AMU 1982; MNR 1994; RPMT 1997; KCET 2000; Orissa JEE 2005]

(a) $NaCl$ (b) $MgCl_2$

(c) $AlCl_3$ (d) $SnCl_4$

25. In the equilibrium $HClO_4 + H_2O \rightleftharpoons H_2O^+ + ClO_4^-$

[BHU 1981, 86]

(a) $HClO_4$ is the conjugate acid of H_2O

(b) H_2O is the conjugate acid of H_3O^+

(c) H_3O^+ is the conjugate base of H_2O

(d) ClO_4^- is the conjugate base of $HClO_4$

26. Which of the following would be expected to form ionic solution in water **[CPMT 1976; Kurukshetra CEE 1998]**

(a) CCl_4 (b) O_2

(c) $NaBr$ (d) $CHBr_3$

27. A solution of sodium bicarbonate in water turns

[NCERT 1971]

(a) Phenolphthalein pink (b) Methyl orange yellow

(c) Methyl orange red (d) Blue litmus red

28. Accepting the definition that an acid is a proton donor, the acid in the following reaction $NH_3 + H_2O \rightarrow NH_4^+ + OH^-$ is **[Kerala (Med.) 2003]**

(a) NH_3 (b) H^+

(c) NH_4^+ (d) H_2O

29. With reference to protonic acids, which of the following statements is correct **[CPMT 1990]**

(a) PH_3 is more basic than NH_3

(b) PH_3 is less basic than NH_3

(c) PH_3 is equally basic as NH_3

(d) PH_3 is amphoteric while NH_3 is basic

30. NH_4OH is weak base because **[CPMT 1979]**

(a) It has low vapour pressure

(b) It is only slightly ionized

(c) It is not a hydroxide of metal

(d) It has low density

31. HNO_3 in liquid hydrogen fluoride behaves

(a) As an acid

(b) As a base

(c) Neither as a base nor as an acid

(d) As a base and as an acid

32. Aqueous solution of $CuSO_4.5H_2O$ changes blue litmus paper to red due to **[CPMT 1979; MP PMT 1989]**

(a) Presence of Cu^{++} ions

(b) Presence of SO_4^{--} ions

(c) Hydrolysis taking place

(d) Reduction taking place

33. In the following reaction

$$HC_2O_4^- + PO_4^{---} \rightleftharpoons HPO_4^{--} + C_2O_4^{--}$$

Which are the two Bronsted bases **[MP PMT 1991]**

(a) $HC_2O_4^-$ and PO_4^{---} (b) HPO_4^{--} and $C_2O_4^{--}$

(c) $HC_2O_4^-$ and HPO_4^{--} (d) PO_4^{---} and $C_2O_4^{--}$

34. Which of the following is the weakest acid **[CPMT 2001]**

(a) HF (b) HCl

(c) HBr (d) HI

35. The degree of dissociation in a weak electrolyte increases

[CBSE PMT 1989; MP PMT 1997]

(a) On increasing dilution (b) On increasing pressure

(c) On decreasing dilution (d) None of these

36. H^+ is a **[MADT Bihar 1983]**

(a) Lewis acid (b) Lewis base

(c) Bronsted-Lowry base (d) None of the above

37. Dissociation of H_3PO_4 takes place in following steps

[CPMT 1976; NCERT 1987]

(a) 1 (b) 2

(c) 3 (d) 4

38. The aqueous solution of disodium hydrogen phosphate is

[MADT Bihar 1982]

(a) Acidic (b) Neutral

(c) Basic (d) None

39. Which of the following is a conjugated acid-base pair

[MADT Bihar 1984; DPMT 2001]

(a) $HCl, NaOH$ (b) NH_4Cl, NH_4OH

(c) H_2SO_4, HSO_4^- (d) KCN, HCN

40. The solution of strong acid and weak base $(FeCl_3)$ is **[MADT Bihar 1981; CPMT 1979, 83, 84]**

(a) Acidic (b) Basic

(c) Neutral (d) None of the above

41. The conjugate acid of HPO_3^{2-} is **[EAMCET 1989]**

(a) H_3PO_4 (b) H_3PO_3

(c) $H_2PO_3^-$ (d) PO_4^{3-}

42. What name is given to the reaction between hydrogen ion and hydroxyl ion **[MP PMT 1990]**

(a) Hydrogenation (b) Hydroxylation

(c) Hydrolysis (d) Neutralization

43. Among the following, the weakest Lewis base is **[NCERT 1981]**

(a) H^- (b) OH^-

(c) Cl^- (d) HCO_3^-

44. The pKa for acid *A* is greater than pKa for acid *B*. The strong acid is **[DPMT 2000]**

(a) Acid *B* (b) Acid *A*

(c) Both *A* and *B* (d) Neither *A* nor *B*

45. The conjugate acid of NH_2^- is **[IIT 1985; Roorkee 1995; EAMCET 1997;CBSE PMT PMT 2000; MP PET 1996,2000]**

(a) NH_3 (b) NH_4^+

(c) NH_2OH (d) N_2H_4

46. Correct statement is **[CPMT 1985]**

(a) NH_4Cl gives alkaline solution in water

(b) CH_3COONa gives acidic solution in water

(c) CH_3COOH is a weak acid

(d) NH_4OH is a strong base

47. pK_a of a weak acid is defined as **[JIPMER 1999]**

(a) $\log_{10} K_a$ (b) $\frac{1}{\log_{10} K_a}$

(c) $\log_{10} \frac{1}{K_a}$ (d) $-\log_{10} \frac{1}{K_a}$

48. A salt $'X'$ is dissolved in water $(pH = 7)$, the resulting solution becomes alkaline in nature. The salt is made of **[CPMT 1983]**

(a) A strong acid and strong base

(b) A strong acid and weak base

(c) A weak acid and weak base

(d) A weak acid and strong base

49. Which one is not an acid salt **[MNR 1984]**

(a) NaH_2PO_2 (b) NaH_2PO_3

(c) NaH_2PO_4 (d) None

50. A white substance was alkaline in solution. Which of the following substances could it be **[CPMT 1989]**

(a) Fe_2O_3 (b) Na_2CO_3

(c) NH_4Cl (d) $NaNO_3$

51. An aqueous solution of ammonium carbonate is **[MP PMT 1989]**

(a) Weakly acidic (b) Weakly basic

(c) Strongly acidic (d) Neither acidic nor basic

52. $100\,ml$ of $0.2\ M\ H_2SO_4$ is added to $100\,ml$ of $0.2\ M\ NaOH$. The resulting solution will be **[BHU 1996]**

(a) Acidic (b) Basic

(c) Neutral (d) Slightly basic

53. H_3BO_3 is **[IIT Screening 2003]**

(a) Monobasic and weak Lewis acid

(b) Monobasic and weak Bronsted acid

(c) Monobasic and strong Lewis acid

(d) Tribasic and weak Bronsted acid

54. In the reaction $SnCl_2 + 2Cl^- \rightarrow SnCl_4$, Lewis acid is **[EAMCET 1987]**

(a) $SnCl_2$ (b) Cl^-

(c) $SnCl_4$ (d) None of these

55. Lewis base is **[RPMT 1997]**

(a) CO_2 (b) SO_3

(c) SO_2 (d) ROH

56. $10\,ml$ of $1\,M\ H_2SO_4$ will completely neutralise

(a) $10\,ml$ of $1\ M\ NaOH$ solution

(b) $10\,ml$ of $2\ M\ NaOH$ solution

(c) $5\ ml$ of $2\ M\ KOH$ solution

(d) $5\ ml$ of $1\ M\ Na_2CO_3$ solution

57. Which of the following compounds are diprotic **[Pb. PMT 2000]**

(a) H_2PO_5 (b) H_2S

(c) $HClO_3$ (d) H_3PO_3

58. When 100 *ml* of 1*M* $NaOH$ solution is mixed with 10 *ml* of 10 *M* H_2SO_4, the resulting mixture will be **[AMU 2002]**

(a) Acidic (b) Alkaline

(c) Neutral (d) Strongly alkaline

59. The pH indicators are **[KCET 1996]**

(a) Salts of strong acids and strong bases

(b) Salts of weak acids and weak bases

(c) Either weak acids or weak bases

(d) Either strong acids or strong bases

60. Which of the following is not Lewis acid **[BHU 1997]**

(a) BF_3 (b) $AlCl_3$
(c) $FeCl_3$ (d) PH_3

61. A solution of sodium acetate in water will **[MNR 1979]**
(a) Turn red litmus blue (b) Turn blue litmus red
(c) Not effect litmus (d) Decolourises litmus

62. Cl^- is the conjugate base of **[NCERT 1979; CPMT 1976; MP PET/PMT 1988]**
(a) $HClO_4$ (b) HCl
(c) $HOCl$ (d) $HClO_3$

63. Which of the following behaves as both Lewis and Bronsted base **[MP PMT 2003]**
(a) BF_3 (b) Cl^-
(c) CO (d) None of these

64. The conjugate acid of a strong base is a **[EAMCET 1979]**
(a) Strong acid (b) Weak acid
(c) Strong base (d) Weak base

65. Which one is the weakest acid **[DPMT 2002]**
(a) HNO_3 (b) $HClO_4$
(c) H_2SO_4 (d) HBr

66. Conjugate base of HPO_4^{2-} is **[MP PMT 1995]**
(a) PO_4^{3-} (b) $H_2PO_4^-$
(c) H_3PO_4 (d) H_4PO_3

67. Which of the following is not Lewis acid **[RPET/PMT 2002]**
(a) $FeCl_3$ (b) $AlCl_3$
(c) BCl_3 (d) NH_3

68. (i) A strong acid has a weak conjugate base
(ii) An acid is an electron pair acceptor
The above statements (i) and (ii)
(a) Correct
(b) Wrong
(c) (i) Correct and (ii) Wrong
(d) (i) Wrong and (ii) Correct

69. The *pH* is less than 7, of the solution of **[Pb. PMT 2002; MP PMT 2003]**
(a) $FeCl_3$ (b) $NaCN$
(c) $NaOH$ (d) $NaCl$

70. In the reaction $I_2 + I^- \rightarrow I_3^-$, the Lewis base is **[CPMT 1997; RPMT 2002; BCECE 2005]**
(a) I_2 (b) I^-
(c) I_3^- (d) None of these

71. The strength of an acid depends on its tendency to **[UPSEAT 2001]**
(a) Accept protons (b) Donate protons
(c) Accept electrons (d) Donate electrons

72. In Lewis acid-base theory, neutralization reaction may be considered as **[NCERT 1977]**
(a) Formation of salt and water
(b) Competition for protons by acid and base
(c) Oxidation reduction
(d) Coordinate covalent bond formation

73. The salt that forms neutral solution in water is **[EAMCET 1981]**
(a) NH_4Cl (b) $NaCl$
(c) Na_2CO_3 (d) K_3BO_3

74. Which of the following cannot act as a Lewis or Bronsted acid **[DCE 2001]**
(a) BF_3 (b) $AlCl_3$
(c) $SnCl_4$ (d) CCl_4

75. Which one of the following salts gives an acidic solution in water **[MP PET 2002]**
(a) CH_3COONa (b) NH_4Cl
(c) $NaCl$ (d) CH_3COONH_4

76. Which of the anhydrous salts when come in contact with water turns blue **[AMU 1981, 82]**
(a) Ferrous sulphate (b) Copper sulphate
(c) Zinc sulphate (d) Cobalt sulphate

77. The species among the following, which can act as an acid and a base is **[AIEEE 2002; KCET 2005]**
(a) HSO_4^- (b) SO_4^{2-}
(c) H_3O^+ (d) Cl^-

78. The strongest base from the following species is **[KCET 1996]**
(a) NH^{2-} (b) OH^-
(c) O^{2-} (d) S^{2-}

79. Which one is Lewis acid **[CPMT 1997]**
(a) Cl^- (b) Ag^+
(c) C_2H_5OH (d) S^{2-}

80. The conjugate acid of $H_2PO_4^-$ is **[MP PET 1990]**
(a) H_3PO_4 (b) $H_2PO_4^-$
(c) PO_4^{3-} (d) H_3O^+

81. The conjugate acid of $S_2O_8^{2-}$ is **[EAMCET 1984]**
(a) $H_2S_2O_8$ (b) H_2SO_4
(c) HSO_4^- (d) $HS_2O_8^-$

82. In the reaction $BCl_3 + PH_3 \rightarrow Cl_3B - PH_3$, Lewis base is **[EAMCET 1986]**
(a) BCl_3 (b) PH_3
(c) $Cl_3B - PH_3$ (d) None of these

83. Which of the following statement is true **[MP PMT 1996]**
(a) The conjugate base of a strong acid is a strong base

(b) The conjugate base of a weak acid is a strong base
(c) The conjugate base of a weak acid is a weak base
(d) The base and its conjugate acid react to form a neutral solution

84. What is the conjugate base of OH^- **[AIEEE 2005]**
(a) O_2
(b) H_2O
(c) O^-
(d) O^{2-}

85. Which of the following is a Lewis base **[BHU 1995]**
(a) CH_4
(b) C_2H_5OH
(c) Acetone
(d) Secondary amine

86. The correct order of acid strength is **[CBSE PMT 2005]**
(a) $HClO < HClO_2 < HClO_3 < HClO_4$
(b) $HClO_4 < HClO < HClO_2 < HClO_3$
(c) $HClO_2 < HClO_3 < HClO_4 < HClO$
(d) $HClO_4 < HClO_3 < HClO_2 < HClO$

87. The strongest acid is **[DPMT 2000]**
(a) H_3AsO_4
(b) H_3AsO_3
(c) H_3PO_3
(d) H_3PO_4

88. Which of the following is the strongest base **[Roorkee 2000]**
(a) $C_2H_5^-$
(b) $C_2H_5COO^-$
(c) $C_2H_5O^-$
(d) OH^-

89. The aqueous solution of which one of the following is basic **[MP PMT 2001]**
(a) $HOCl$
(b) $NaHSO_4$
(c) NH_4NO_3
(d) $NaOCl$

90. Which of the following is the weakest base **[IIT 1980]**
(a) $NaOH$
(b) $Ca(OH)_2$
(c) NH_4OH
(d) KOH

91. The suitable indicator for strong acid and weak base is **[RPMT 1997; UPSEAT 2002]**
(a) Methyl orange
(b) Methyl red
(c) Phenol red
(d) Phenolphthalein

92. Among the following acids, the weakest one is **[NCERT 1984]**
(a) HF
(b) HCl
(c) HBr
(d) HI

93. The compound HCl behaves as …. in the reaction, $HCl + HF \rightarrow H_2^+Cl + F^-$ **[JIPMER 2001]**
(a) Weak base
(b) Weak acid
(c) Strong base
(d) Strong acid

94. The conjugate base of a strong acid is a **[EAMCET 1978]**
(a) Strong base
(b) Strong acid
(c) Weak acid
(d) Weak base

95. Which among the following is strongest acid **[BHU 2005]**
(a) $H(ClO)O_2$
(b) $H(ClO)O_3$
(c) $H(ClO)O$
(d) $H(ClO)$

96. In the reaction $2H_2O \rightleftarrows H_3O^+ + OH^-$, water is **[MP PET 1989]**
(a) A weak base
(b) A weak acid
(c) Both a weak acid and a weak base
(d) Neither an acid nor a base

97. In the reaction $HCl + H_2O \rightleftharpoons H_3O^+ + Cl^-$ **[NCERT 1978; EAMCET 1982, 89]**
(a) H_2O is the conjugate base of HCl acid
(b) Cl^- is the conjugate base of HCl acid
(c) Cl^- is the conjugate acid of H_2O base
(d) H_3O^+ is the conjugate base of HCl

98. According to Lewis concept, an acid is a substance which **[EAMCET 1981; NCERT 1981; CPMT 1986; MP PMT 1987]**
(a) Accepts protons
(b) Donates protons
(c) Accepts a lone pair of electrons
(d) Donates a lone pair of electrons

99. Water is a **[KCET 2002]**
(a) Amphoteric acid
(b) Aprotic solvent
(c) Protophobic solvent
(d) None of these

100. Conjugate base of NH_3 is **[RPMT 2002]**
(a) $NH_4^{\oplus}$
(b) $NH_2^{\oplus}$
(c) $NH_2^{\ominus}$
(d) N_2

101. Which of the following species is an acid and also a conjugate base of another acid **[NCERT 1981]**
(a) HSO_4^-
(b) H_2SO_4
(c) OH^-
(d) H_3O^+

102. Which of the following is Lewis acid **[NCERT 1978; EAMCET 1987; MP PET 1994; CPMT 1990; AFMC 1997; RPMT 1999]**
(a) BF_3
(b) Cl^-
(c) H_2O
(d) NH_3

103. According to Bronsted-Lowry concept, base is a substance which is **[NCERT 1982; RPMT 1997 AFMC 1999]**
(a) A proton donor
(b) An electron pair acceptor
(c) A proton acceptor
(d) An electron pair donor

104. Which of the following is known as hydronium ion

[NCERT 1976]

(a) H^+ (b) H_2O^+

(c) H_3O^+ (d) $H_2O_2^+$

105. An aqueous solution of aluminium sulphate would show **[NCERT 1977]**

(a) An acidic reaction

(b) A neutral reaction

(c) A basic reaction

(d) Both acidic and basic reaction

106. The aqueous solution of aluminium chloride is acidic due to **[MNR 1986, 88]**

(a) Cation hydrolysis

(b) Anion hydrolysis

(c) Hydrolysis of both anion and cation

(d) Dissociation

107. HSO_4^- is the conjugate base of **[NCERT 1977]**

(a) H^+ (b) H_2SO_3

(c) SO_4^{2-} (d) H_2SO_4

108. An acid is a compound which furnishes (Bronsted-Lowry concept) **[EAMCET 1975]**

(a) An electron (b) A proton

(c) An electron and a proton (d) None of the above

109. The conjugate base of sulphuric acid is **[EAMCET 1974]**

(a) Sodium hydroxide (b) Hydrochloric acid

(c) Bisulphate ion (d) Barium hydroxide

110. Which is strongest Lewis base **[CPMT 1994]**

(a) SbH_3 (b) AsH_3

(c) PH_3 (d) NH_3

111. According to Bronsted principle, an aqueous solution of HNO_3 will contain **[MP PMT/PET 1988]**

(a) NO_2^- (b) NO_3^-

(c) NO_2^+ (d) NO^+

112. Aqueous solution of an acid is characterised by the presence of **[NCERT 1977]**

(a) H^+ ions (b) H_2^+ ions

(c) H_3O^+ ions (d) H_4O^+ ions

113. Ammonium ion is **[RPMT 1999; KCET 2002]**

(a) Neither an acid nor base (b) Both an acid and a base

(c) A conjugate acid (d) A conjugate base

114. Aqueous solution of $AlCl_3$ is **[RPMT 2002]**

(a) Acidic (b) Basic

(c) Amphoteric (d) None of these

115. The species which acts as a Lewis acid but not a Bronsted acid is **[MP PMT 1999; Kurukshetra CET 2002]**

(a) NH_2^- (b) O^{2-}

(c) BF_3 (d) OH^-

116. Among the following, the weakest base is **[MP PMT 2002]**

(a) H^- (b) CH_3^-

(c) CH_3O^- (d) Cl^-

117. Which of the following is not lewis base **[EAMCET 1975; RPMT 2002]**

(a) NH_3 (b) PH_3

(c) $(CH_3)_3N$ (d) HN_3

118. pK_a value of the strongest acid among the following is **[MP PMT 1990]**

(a) 3.0 (b) 4.5

(c) 1.0 (d) 2.0

119. The most acidic compound in water is **[CBSE PMT 2001]**

(a) $AlCl_3$ (b) $BeCl_2$

(c) $FeCl_3$ (d) None of these

120. BF_3 is used as a catalyst in several industrial processes due to its **[Kerala (Med.) 2002]**

(a) Strong reducing agent

(b) Weak reducing agent

(c) Strong Lewis acid nature

(d) Weak Lewis acid character

121. The aqueous solution of $AlCl_3$ is acidic due to the hydrolysis of **[UPSEAT 2001, 02]**

(a) Aluminium ion

(b) Chloride ion

(c) Both aluminium and chloride ion

(d) None of these

122. Which shows weak ionisation in water **[MH CET 2001]**

(a) H_2SO_4 (b) $NaCl$

(c) HNO_3 (d) NH_3

123. An organic dye, cosine used to detect end point of precipitation titration by adsorption is called **[MH CET 1999]**

(a) Absorption indicator (b) Adsorption indicator

(c) Chemical indicator (d) None of these

124. The indicator used in the titration of iodine against sodium thiosulphate is **[AFMC 2002]**

(a) Starch (b) $K_3Fe(CN)_6$

(c) K_2CrO_4 (d) Potassium

125. Phenolphthalein does not act as an indicator for the titration between **[Pb. PMT 2002]**

(a) $NaOH$ and CH_3COOH

(b) $H_2C_2O_4$ and $KMnO_4$

(c) $Ba(OH)_2$ and HCl

(d) KOH and H_2SO_4

126. Which is not example of Bronsted Lowry theory **[AIEEE 2003]**

(a) $AlCl_3$
(b) H_2SO_4
(c) SO_2
(d) HNO_3

127. An aqueous solution of sodium carbonate is alkaline because sodium carbonate is a salt of **[MP PET 2002]**

(a) Weak acid and weak base
(b) Strong acid and weak base
(c) Weak acid and strong base
(d) Strong acid and strong base

128. The acid that results when a base accepts a proton is called **[Kerala (Med.) 2002]**

(a) Conjugate base of the acid
(b) Conjugate protonated base
(c) Lewis base
(d) Conjugate acid of the base
(e) None of these

129. Ammonia gas dissolves in water to form NH_4OH. In this reaction water acts as **[KCET (Engg./Med.) 1999]**

(a) A conjugate base
(b) A non-polar solvent
(c) An acid
(d) A base

130. The conjugate base in the following reaction

$H_2SO_4 + H_2O \rightleftarrows H_3O^+ + HSO_4^-$ **[DCE 1999]**

(a) H_2O
(b) HSO_4^-
(c) H_3O^+
(d) SO_2

131. An aqueous solution of aluminium sulphate shows **[DPMT 2001]**

(a) A basic nature
(b) An acidic nature
(c) A neutral nature
(d) Both acidic and basic nature

132. Neutralization of an acid with a base invariably results in the production of **[CPMT 1983]**

(a) H_3O^+
(b) OH^-
(c) H_2O
(d) H^+ and OH^-

133. The conjugate acid of HPO_4^{2-} is **[MP PMT 1987, 90, 91; EAMCET 1993]**

(a) $H_2PO_4^-$
(b) PO_4^{3-}
(c) H_3PO_4
(d) H_3PO_3

134. Which of the following is not used as a Lewis acid **[MP PET 2000]**

(a) $SnCl_4$
(b) $FeCl_3$
(c) KCl
(d) BF_3

135. Orthoboric acid in aqueous medium is **[AMU 2000]**

(a) Monobasic
(b) Dibasic
(c) Tribasic
(d) All are correct

136. According to Lewis concept which one of the following is not a base **[MP PET/PMT 1988; Pb. CET 2003]**

(a) OH^-
(b) H_2O
(c) Ag^+
(d) NH_3

137. The aqueous solution of ammonium chloride is **[CPMT 1987]**

(a) Neutral
(b) Basic
(c) Acidic
(d) Amphoteric

138. In the process $BCl_3 + PH_3 \rightarrow BCl_3 : PH_3$ The Lewis acid is **[RPMT 2000]**

(a) PH_3
(b) BCl_3
(c) Both
(d) None

139. The conjugate acid of NH_3 is **[BHU Varanasi 1999; Pb. PMT 2004]**

(a) NH_3
(b) NH_4^+
(c) N_2H_4
(d) NH_2OH

140. Which halide of nitrogen is least basic **[DPMT 2001]**

(a) NBr_3
(b) NI_3
(c) NCl_3
(d) NF_3

141. When $FeCl_3$ gets soluble in water, then its solution represents which of the characteristics **[MP PET/PMT 1988]**

(a) Amphoteric
(b) Acidic
(c) Basic
(d) Neutral

142. Lewis acid are those substances **[MP PMT 1987]**

(a) Which accept electron pair
(b) Which provide H^+ ion in the solution
(c) Which give electron pair
(d) Which accept OH^- ion

143. The conjugate base of HCO_3^- is

(a) H_2CO_3
(b) CO_3^{2-}
(c) CO_2
(d) H_2O

144. In the reaction $NH_3 + BF_3 \rightleftharpoons NH_3 \rightarrow BF_3$, BF_3 is **[MP PMT 1989; MHCET 2001]**

(a) Lewis acid
(b) Lewis base

(c) Neither Lewis acid nor Lewis base
(d) Lewis acid and Lewis base both

145. The strongest Lewis base in the following **[MP PET/PMT 1988]**

(a) CH_3^- (b) F^-
(c) NH_2^- (d) OH^-

146. The aqueous solution of $CuSO_4$ is **[CPMT 1985]**

(a) Acidic (b) Basic
(c) Neutral (d) Amphoteric

147. The acid having the highest pK_a value among the following is **[JIPMER 2002]**

(a) $HCOOH$ (b) CH_3COOH
(c) $ClCH_2COOH$ (d) FCH_2COOH

148. The indicator used in the titration of sodium carbonate with sulphuric acid is **[DPMT 2001]**

(a) Phenolphthalein
(b) Methyl orange
(c) Potassium ferrocynide
(d) Potassium ferricynide

149. According to Bronsted law, water is a/an **[MP PET/PMT 1988]**

(a) Base (b) Acid
(c) Acid and base both (d) Salt

150. Which of the following can give base OH^- **[MP PET/PMT 1988]**

(a) H_2O (b) H_3O^+
(c) H_2 (d) HCl

151. Conjugate base of HBr is **[MP PET/PMT 1988]**

(a) H_2Br^+ (b) H^+
(c) Br^- (d) Br^+

152. Molar heat of neutralization of $NaOH$ with HCl in comparison to that of KOH with HNO_3 is **[MP PMT 1989]**

(a) Less (b) More
(c) Equal (d) Depends on pressure

153. Which of the following is not a Lewis acid **[J & K 2005]**

(a) BF_3 (b) $AlCl_3$
(c) HCl (d) $LiAlH_4$

154. The solvent which neither accepts proton nor donates proton is called **[RPMT 2000]**

(a) Amphoteric (b) Neutral
(c) Aprotic (d) Amphiprotic

155. For the reaction in aqueous solution $Zn^{2+} + X^- \rightleftarrows ZnX^+$, the K_{eq} is greatest when X is **[Pb. PMT 1998]**

(a) F^- (b) NO_3^-
(c) ClO_4^- (d) I^-

156. Why are strong acids generally used as standard solutions in acid-base titrations **[Pb. PMT 1998]**

(a) The pH at the equivalence point will always be 7
(b) They can be used to titrate both strong and weak bases
(c) Strong acids form more stable solutions than weak acids
(d) The salts of strong acids do not hydrolysed

157. For an aqueous solution, the characteristic species of acid is **[RPMT 1999]**

(a) H^+ ion (b) H_3O^+ ion
(c) H_2^+ ion (d) H_4O^+ ion

158. Which is a Lewis base **[CPMT 1988; JEE Orissa 2004]**

(a) B_2H_6 (b) $LiAlH_4$
(c) AlH_3 (d) NH_3

159. For a weak acid, the incorrect statement is **[Pb. PMT 2004]**

(a) Its dissociation constant is low
(b) Its pK_a is very low
(c) It is partially dissociated
(d) Solution of its sodium salt is alkaline in water

160. Boron halides behave as Lewis acids, because of their **[CBSE PMT 1996; BHU 2004]**

(a) Ionic nature (b) Acidic nature
(c) Covalent nature (d) Electron deficient nature

161. Would gaseous *HCl* be considered as an Arrhenius acid **[UPSEAT 2004]**

(a) Yes
(b) No
(c) Not known
(d) Gaseous *HCl* does not exist

162. Which one of the following is called amphoteric solvent **[UPSEAT 2004]**

(a) Ammonium hydroxide (b) Chloroform
(c) Benzene (d) Water

163. Strongest conjugate base is **[DPMT 2004]**

(a) Cl^- (b) Br^-
(c) F^- (d) I^-

164. The conjugate base of $H_2PO_4^-$ is **[AIEEE 2004]**

(a) H_3PO_4 (b) P_2O_5

(c) PO_4^{3-} (d) HPO_4^{2-}

165. Conjugate base of HSO_4^- is **[MH CET 2004]**

(a) SO_4^{2-} (b) H_2SO_4

(c) $H_3SO_4^+$ (d) None of these

Common ion effect, Isohydric solutions, Solubility product, Ionic product of water and Salt hydrolysis

1. The expression for the solubility product of $Al_2(SO_4)_3$ is

(a) $K_{sp}=[Al^{3+}](SO_4^{2-}]$ (b) $K_{sp}=[Al^{3+}]^2(SO_4^{2-}]^3$

(c) $K_{sp}=[Al^{3+}]^3(SO_4^{2-}]^2$ (d) $K_{sp}=[Al^{3+}]^2(SO_4^{2-}]^2$

2. On addition of ammonium chloride to a solution of ammonium hydroxide **[CPMT 1976, 80, 81, 99; NCERT 1976, 77; MP PMT 1989, 99; DPMT 1983]**

(a) Dissociation of NH_4OH increases

(b) Concentration of OH^- increases

(c) Concentration of OH^- decreases

(d) Concentration of NH_4^+ and OH^- increases

3. The solubility product of a salt having general formula MX_2, in water is : 4×10^{-12}. The concentration of M^{2+} ions in the aqueous solution of the salt is **[AIEEE 2005]**

(a) $2.0\times10^{-6}M$ (b) $1.0\times10^{-4}M$

(c) $1.6\times10^{-4}M$ (d) $4.0\times10^{-10}M$

4. In a saturated solution of electrolyte, the ionic product of their concentration are constant at constant temperature and this constant for electrolyte is known as **[CPMT 1983]**

(a) Ionic product (b) Solubility product

(c) Ionization constant (d) Dissociation constant

5. If the solubility product K_{sp} of a sparingly soluble salt MX_2 at $25^\circ C$ is 1.0×10^{-11}, the solubility of the salt in *mole litre*$^{-1}$ at this temperature will be **[RPMT 2000]**

(a) 2.46×10^{14} (b) 1.36×10^{-4}

(c) 2.60×10^{-7} (d) 1.20×10^{-10}

6. The unit of ionic product of water K_w are **[UPSEAT 2001, 02]**

(a) $Mol^{-1}L^{-1}$ (b) $Mol^{-2}L^{-2}$

(c) $Mol^{-2}L^{-1}$ (d) Mol^2L^{-2}

7. A solution which is $10^{-3}M$ each in $Mn^{2+}, Fe^{2+}, Zn^{2+}$ and Hg^{2+} is treated with $10^{-16}M$ sulphide ion. If K_{sp} of MnS, FeS, ZnS and HgS are $10^{-15}, 10^{-23}, 10^{-20}$ and 10^{-54} respectively, which one will precipitate first **[IIT Screening 2003]**

(a) FeS (b) MgS

(c) HgS (d) ZnS

8. Let the solubility of an aqueous solution of $Mg(OH)_2$ be *x* then its k_{sp} is **[AIEEE 2002]**

(a) $4x^3$ (b) $108x^5$

(c) $27x^4$ (d) $9x$

9. The solubility product of $BaSO_4$ at $25^\circ C$ is 1.0×10^{-9}. What would be the concentration of H_2SO_4 necessary to precipitate $BaSO_4$ from a solution of $0.01M\ Ba^{2+}$ ions **[RPMT 1999]**

(a) 10^{-9} (b) 10^{-8}

(c) 10^{-7} (d) 10^{-6}

10. The solubility in water of a sparingly soluble salt AB_2 is $1.0\times10^{-5}\,mol\,l^{-1}$. Its solubility product number will be **[AIEEE 2003]**

(a) 4×10^{-15} (b) 4×10^{-10}

(c) 1×10^{-15} (d) 1×10^{-10}

11. The solubility of CaF_2 is a *moles/litre*. Then its solubility product is ..... **[Orissa JEE 2002]**

(a) s^2 (b) $4s^3$

(c) $3s^2$ (d) s^3

12. On passing a current of HCl gas in a saturated solution of $NaCl$, the solubility of $NaCl$ **[CPMT 1989; CBSE PMT 1989]**

(a) Increases (b) Decreases

(c) Remains unchanged (d) $NaCl$ decomposes

13. Which is the correct representation of the solubility product constant of Ag_2CrO_4 **[NCERT 1974, 75]**

(a) $[Ag^+]^2[CrO_4^{-2}]$ (b) $[Ag^+][CrO_4^{-2}]$

(c) $[2Ag^+][CrO_4^{-2}]$ (d) $[2Ag^+]^2[CrO_4^{-2}]$

14. The solubility of CaF_2 is 2×10^{-4} *moles/litre*. Its solubilily product (K_{sp}) is **[NCERT 1981; BHU 1983, 86; MP PET 1992; CBSE PMT 1999]**

(a) 2.0×10^{-4} (b) 4.0×10^{-3}

(c) 8.0×10^{-12} (d) 3.2×10^{-11}

15. Solubility product of a sulphide *MS* is 3×10^{-25} and that of another sulphide *NS* is 4×10^{-40}. In ammoniacal solution **[NCERT 1981]**

(a) Only *NS* gets precipitated

(b) Only MS gets precipitated
(c) No sulphide precipitates
(d) Both sulphides precipitate

16. Which of the following salts when dissolved in water will get hydrolysed
[MNR 1985; CPMT 1989; CBSE PMT 1989; MP PET 1999]
(a) $NaCl$ (b) NH_4Cl
(c) KCl (d) Na_2SO_4

17. The aqueous solution of $FeCl_3$ is acidic due to
[CPMT 1972, 79, 83, 84; MP PET/PMT 1988; RPMT 2000]
(a) Acidic impurities (b) Ionisation
(c) Hydrolysis (d) Dissociation

18. A precipitate of $AgCl$ is formed when equal volumes of the following are mixed. $[K_{sp}$ for $AgCl = 10^{-10}]$ **[KCET 2005]**
(a) $10^{-4} M\ AgNO_3$ and $10^{-7} M\ HCl$
(b) $10^{-5} M\ AgNO_3$ and $10^{-6} M\ HCl$
(c) $10^{-5} M\ AgNO_3$ and $10^{-4} M\ HCl$
(d) $10^{-6} M\ AgNO_3$ and $10^{-6} M\ HCl$

19. The solubility of silver chromate in 0.01 M K_2CrO_4 is $2 \times 10^{-8} mol dm^{-3}$. The solubility product of silver chromate will be
[MH CET 2000]
(a) 8×10^{-24} (b) 16×10^{-24}
(c) 1.6×10^{-18} (d) 16×10^{-18}

20. Some salts although containing two different metallic elements give test for only one of them in solution. Such salts are **[MNR 1979]**
(a) Double salts (b) Normal salts
(c) Complex salts (d) Basic salts

21. What is the pH value of $\frac{N}{1000} KOH$ solution
[CPMT 1975; MNR 1986, 91; Pb. CET 2004]
(a) 10^{-11} (b) 3
(c) 2 (d) 11

22. Mohr's salt is a **[MNR 1986]**
(a) Normal salt (b) Acid salt
(c) Basic salt (d) Double salt

23. Aqueous solution of sodium acetate is
[MNR 1978; CPMT 1971, 80, 81; MADT Bihar 1982; MP PMT 1985;]
(a) Neutral (b) Weakly acidic
(c) Strongly acidic (d) Alkaline

24. Which is the correct alternate for hydrolysis constant of NH_4CN **[CBSE PMT 1989]**
(a) $\sqrt{\frac{K_w}{K_a}}$ (b) $\frac{K_w}{K_a \times K_b}$
(c) $\sqrt{\frac{K_b}{c}}$ (d) $\frac{K_a}{K_b}$

25. Which of the following salts undergoes hydrolysis
[CPMT 1972, 74, 78; DPMT 1985]
(a) CH_3COONa (b) KNO_3
(c) $NaCl$ (d) K_2SO_4

26. What will happen if CCl_4 is treated with $AgNO_3$
[DPMT 1983]
(a) A white ppt. of $AgCl$ will form
(b) NO_2 will be evolved
(c) CCl_4 will dissolve in $AgNO_3$
(d) Nothing will happen

27. The correct representation for solubility product of SnS_2 is
[CPMT 1977; MP PET 1999;RPMT 2000]
(a) $[Sn^{4+}][S^{2-}]^2$ (b) $[Sn^{2+}][S^{2-}]^2$
(c) $[Sn^{2+}][2S^{2-}]$ (d) $[Sn^{4+}][2S^{2-}]^2$

28. A precipitate of calcium oxalate will not dissolve in
[CPMT 1971, 89; IIT 1986]
(a) HCl (b) HNO_3
(c) Aquaregia (d) CH_3COOH

29. Baking soda is **[RPMT 2000]**
(a) Basic salt (b) Acidic salt
(c) Complex salt (d) Double salt

30. Which one of the following substances will be a mixed salt
[DPMT 1982; CPMT 1972]
(a) $NaHCO_3$
(b) $Ca(OCl)Cl$
(c) $K_2SO_4Al_2(SO_4)_3.24H_2O$
(d) $Mg(OH)Br$

31. Solubility product of $BaCl_2$ is 4×10^{-9}. Its solubility in moles/litre would be
[AFMC 1982; Roorkee 1990; BHU 2000]
(a) 1×10^{-3} (b) 1×10^{-9}
(c) 4×10^{-27} (d) 1×10^{-27}

32. Which hydroxide will have lowest value of solubility product at normal temperature (25^oC)
[IIT 1990; RPMT 1997]
(a) $Mg(OH)_2$ (b) $Ca(OH)_2$
(c) $Ba(OH)_2$ (d) $Be(OH)_2$

33. Which will not be hydrolysed **[MP PMT 1989]**
(a) Potassium nitrate
(b) Potassium cyanide
(c) Potassium succinate
(d) Potassium carbonate

34. Which pair will show common ion effect
[MP PMT 1990, 99; Pb. PMT 2001]

(a) $BaCl_2 + Ba(NO_3)_2$
(b) $NaCl + HCl$
(c) $NH_4OH + NH_4Cl$
(d) $AgCN + KCN$

35. Which is least soluble in water **[UPSEAT 1999]**
(a) $AgCl$
(b) AgF
(c) AgI
(d) Ag_2S

36. A white salt is readily soluble in water and gives a colourless solution with a pH of about 9. The salt would be **[Pb. PMT 1998]**
(a) NH_4NO_3
(b) CH_3COONa
(c) CH_3COONH_4
(d) $CaCO_3$

37. If acetic acid mixed with sodium acetate, then H^+ ion concentration will be **[Roorkee 1995]**
(a) Increased
(b) Decreased
(c) Remains unchanged
(d) pH decreased

38. Solubility of $AgCl$ will be minimum in **[CBSE PMT 1995]**
(a) $0.001 M\ AgNO_3$
(b) Pure water
(c) $0.01 M\ CaCl_2$
(d) $0.01 M\ NaCl$

39. In absence of formation of complex ions by the addition of a common ion, the solubility of a given salt is **[BHU 1979]**
(a) Increased
(b) Decreased
(c) Unaffected
(d) First increased and then decreased

40. At 298 *K*, the solubility product of $PbCl_2$ is 1.0×10^{-6}. What will be the solubility of $PbCl_2$ in moles/litre **[MP PMT 1990; CPMT 1985, 96]**
(a) 6.3×10^{-3}
(b) 1.0×10^{-3}
(c) 3.0×10^{-3}
(d) 4.6×10^{-14}

41. Solubility product is **[CET Pune 1998]**
(a) The ionic product of an electrolyte in its saturated solution
(b) The product of the solubilities of the ions of the electrolyte
(c) The product of solubilities of the salts
(d) The product of the concentration of the ions

42. Ionic product of water increases, if **[AMU 1983; MP PET 1986; MP PET/PMT 1988; JIPMER 2002]**
(a) Pressure is reduced
(b) H^+ is added
(c) OH^- is added
(d) Temperature increases

43. Which one is a mixed salt **[DPMT 1985]**
(a) $NaHSO_4$
(b) $NaKSO_4$
(c) $K_4Fe(CN)_6$
(d) $Mg(OH)Cl$

44. If K_{sp} for $HgSO_4$ is 6.4×10^{-5}, then solubility of the salt is **[AFMC 1997; KCET 2000; CPMT 2000; JIPMER 2001]**
(a) 8×10^{-3}
(b) 8×10^{-6}
(c) 6.4×10^{-5}
(d) 6.4×10^{-3}

45. The solubility of $BaSO_4$ in water is $2.33\times10^{-3}\ gm/litre$ Its solubility product will be (molecular weight of $BaSO_4=233$) **[AIIMS 1998]**
(a) 1×10^{-5}
(b) 1×10^{-10}
(c) 1×10^{-15}
(d) 1×10^{-20}

46. The solubility of $AgCl$ in $0.2\ M\ NaCl$ solution (K_{sp} for $AgCl=1.20\times10^{-10}$) is **[MP PET 1996]**
(a) $0.2\ M$
(b) $1.2\times10^{-10}\ M$
(c) $0.2\times10^{-10}\ M$
(d) $6.0\times10^{-10}\ M$

47. The solubility of AgI in NaI solution is less than that in pure water because **[UPSEAT 2001]**
(a) *AgI* forms complex with *NaI*
(b) Of common ion effect
(c) Solubility product of *AgI* is less than that of *NaI*
(d) The temperature of the solution decreases

48. The solubility product of $BaSO_4$ is 1.5×10^{-9}. The precipitation in a 0.01 $M\ Ba^{2+}$ solution will start, on adding H_2SO_4 of concentration **[CPMT 1988]**
(a) $10^{-9} M$
(b) $10^{-8} M$
(c) $10^{-7} M$
(d) $10^{-6} M$

49. At $20^\circ C$, the Ag^+ ion concentration in a saturated solution of Ag_2CrO_4 is $1.5\times10^{-4}\ mole/litre$ At $20^\circ C$, the solubility product of Ag_2CrO_4 would be **[MP PET 1997; MP PMT 1999]**
(a) 3.3750×10^{-12}
(b) 1.6875×10^{-10}
(c) 1.6875×10^{-12}
(d) 1.6875×10^{-11}

50. The solubility of $PbCl_2$ is **[MP PMT 1995; DCE 1999]**
(a) $\sqrt{K_{sp}}$
(b) $\sqrt[3]{K_{sp}}$
(c) $\sqrt[3]{\frac{K_{sp}}{4}}$
(d) $\sqrt{8K_{sp}}$

51. The solubility product of $AgCl$ is 1.44×10^{-4} at $100^\circ C$. The solubility of silver chloride in boiling water may be **[MP PMT 1994; Bihar MEE 1998]**
(a) $0.72\times10^{-4}\ M$
(b) $1.20\times10^{-2}\ M$
(c) $0.72\times10^{-2}\ M$
(d) $1.20\times10^{-4}\ M$

52. If the solubility of a sparingly soluble salt of the type BA_2 (giving three ions on dissociation of a molecule) is X moles per litre, then its solubility product is given by **[BHU 1987]**
(a) x^2
(b) $2x^3$

(c) $4x^2$ (d) $4x^3$

53. The solubility product of Ag_2CrO_4 is 32×10^{-12}. What is the concentration of CrO_4^- ions in that solution

[BHU 1997; DPMT 2004]

(a) $2\times10^{-4}\, m/s$ (b) $16\times10^{-4}\, m/s$

(c) $8\times10^{-4}\, m/s$ (d) $8\times10^{-8}\, m/s$

54. The addition of HCl will not suppress the ionization of

[MP PET 1993]

(a) Acetic acid (b) Benzoic acid

(c) H_2S (d) Sulphuric acid

55. On the addition of a solution containing CrO_4^{2-} ions to the solution of Ba^{2+}, Sr^{2+} and Ca^{2+} ions, the precipitate obtained first will be of **[MP PMT 1993]**

(a) $CaCrO_4$ (b) $SrCrO_4$

(c) $BaCrO_4$ (d) Mixture of (a), (b), (c)

56. The solubility product of a sparingly soluble salt AB at room temperature is 1.21×10^{-6}. Its molar solubility is

[CPMT 1987; MP PET 2001]

(a) 1.21×10^{-6} (b) 1.21×10^{-3}

(c) 1.1×10^{-4} (d) 1.1×10^{-3}

57. The precipitation occurs if ionic concentration is

[AFMC 1995; J & K 2005]

(a) Less than solubility product
(b) More than solubility product
(c) Equal to solubility product
(d) None of these

58. If S and K_{sp} are respectively solubility and solubility product of a sparingly soluble binary electrolyte, then

[CPMT 1988; MP PMT 1999]

(a) $S=K_{sp}$ (b) $S=K_{sp}^2$

(c) $S=\sqrt{K_{sp}}$ (d) $S=\frac{1}{2}K_{sp}$

59. Any precipitate is formed when

[AIIMS 1982; DPMT 1985; KCET 1999; MP PMT 2004]

(a) Solution becomes saturated
(b) The value of ionic product is less that than the value of solubility product
(c) The value of ionic product is equal than the value of solubility product
(d) The value of ionic product is greater than the value of solubility product

60. The solubility product of $AgCl$ is 4.0×10^{-10} at $298\,K$. The solubility of $AgCl$ in $0.04m\ CaCl_2$ will be

[KCET 1996]

(a) $2.0\times10^{-5}\, m$ (b) $1.0\times10^{-4}\, m$

(c) $5.0\times10^{-9}\, m$ (d) $2.2\times10^{-4}\, m$

61. Hydrolysis of sodium acetate will give **[MNR 1978]**

(a) Acidic solution (b) Basic solution

(c) Neutral solution (d) Normal solution

62. If the solubility product of $BaSO_4$ is 1.5×10^{-9} in water, its solubility in moles per litre, is

[BHU 1995; MP PET 1995; UPSEAT 204]

(a) 1.5×10^{-9} (b) 3.9×10^{-5}

(c) 7.5×10^{-5} (d) 1.5×10^{-5}

63. On passing H_2S gas through a highly acidic solution containing Cd^{2+} ions, CdS is not precipitated because

(a) Of common ion effect
(b) The solubility of CdS is low
(c) Cd^{2+} ions do not form complex with H_2S
(d) The solubility product of CdS is low

64. Which of the following will occur if a 0.1 *M* solution of a weak acid is diluted to $0.01M$ at constant temperature

[UPSEAT 2001, 02]

(a) $[H^+]$ will decrease to 0.01 *M*
(b) pH will decrease
(c) Percentage ionization will increase
(d) K_a will increase

65. If solubility of calcium hydroxide is $\sqrt{3}$, then its solubility product will be

[MH CET 2002]

(a) 27 (b) 3

(c) 9 (d) $12\sqrt{3}$

66. When NH_4Cl is added to NH_4OH solution, the dissociation of ammonium hydroxide is reduced. It is due to

[MP PMT 1993]

(a) Common ion effect (b) Hydrolysis

(c) Oxidation (d) Reduction

67. At 298 *K*, the solubility of $PbCl_2$ is $2\times10^{-2}\, mol/lit$, then $k_{sp}=$

[RPMT 2002]

(a) 1×10^{-7} (b) 3.2×10^{-7}

(c) 1×10^{-5} (d) 3.2×10^{-5}

68. The solubility product of silver sulphide is 3.2×10^{-11}. Its solubility at the experimental temperature is

(a) 2×10^{-4} *moles per litre*
(b) 6×10^{-6} *moles per litre*
(c) 1.2×10^{-5} *moles per litre*
(d) 8×10^{-4} *moles per litre*

69. The solubility of $CaCO_3$ in water is $3.05\times10^{-4}\ moles/litre$ Its solubility product will be **[MP PMT 1997]**

(a) 3.05×10^{-4} (b) 10

(c) 6.1×10^{-4} (d) 9.3×10^{-8}

70. Solubility of BaF_2 in a solution $Ba(NO_3)_2$ will be represents by the concentration term **[UPSEAT 2001, 02; CPMT 2002]**

(a) $[Ba^{++}]$ (b) $[F^-]$

(c) $\frac{1}{2}[F^-]$ (d) $2[NO_3^-]$

71. The solubility of $PbCl_2$ at 25^0C is 6.3×10^{-3} *mole/litre*. Its solubility product at that temperature is **[NCERT 1979; CPMT 1985]**

(a) $(6.3\times10^{-3})\times(6.3\times10^{-3})$

(b) $(6.3\times10^{-3})\times(12.6\times10^{-3})$

(c) $(6.3\times10^{-3})\times(12.6\times10^{-3})^2$

(d) $(12.6\times10^{-3})\times(12.6\times10^{-3})$

72. Which of the following cannot be hydrolysed **[MP PMT 1996]**

(a) A salt of weak acid and strong base

(b) A salt of strong acid and weak base

(c) A salt of weak acid and weak base

(d) A salt of strong acid and strong base

73. pH of water is 7. When a substance Y is dissolved in water, the pH becomes 13. The substance Y is a salt of **[MP PMT 1997]**

(a) Strong acid and strong base

(b) Weak acid and weak base

(c) Strong acid and weak base

(d) Weak acid and strong base

74. Which is a basic salt **[MP PMT 1985]**

(a) PbS (b) $PbCO_3$

(c) $PbSO_4$ (d) $2PbCO_3.Pb(OH)_2$

75. The saturated solution of Ag_2SO_4 is $2.5\times10^{-2}\ M$. Its solubility product (K_{sp}) is **[NCERT 1980]**

(a) 62.5×10^{-6} (b) 6.25×10^{-4}

(c) 15.625×10^{-6} (d) 3.125×10^{-6}

76. K_{sp} for sodium chloride is $36\ mol^2/litre^2$. The solubility of sodium chloride is **[BHU 1981]**

(a) $\frac{1}{36}$ (b) $\frac{1}{6}$

(c) 6 (d) 3600

77. Sodium chloride is purified by passing hydrogen chloride gas in an impure solution of sodium chloride. It is based on **[MP PMT 1996]**

(a) Buffer action (b) Common ion effect

(c) Association of salt (d) Hydrolysis of salt

78. If the concentration of lead iodide in its saturated solution at 25^0C be 2×10^{-3} moles per litre, then its solubility product is **[CPMT 1984]**

(a) 4×10^{-6} (b) 8×10^{-12}

(c) 6×10^{-9} (d) 32×10^{-9}

79. The precipitate of CaF_2 $(K_{sp}=1.7\times10^{-10})$ is obtained when equal volumes of the following are mixed **[IIT 1992; UPSEAT 2000]**

(a) $10^{-4}M\ Ca^{2+}+10^{-4}M\ F^-$

(b) $10^{-2}M\ Ca^{2+}+10^{-3}M\ F^-$

(c) Both

(d) None of these

80. In the reaction: $H_2S \rightleftarrows 2H^+ + S^{--}$, when NH_4OH is added, then **[KCET (Med.) 1999; AFMC 2000]**

(a) S^{--} is precipitate

(b) No action takes places

(c) Concentration of S^{--} decreases

(d) Concentration of S^{--} increases

81. What is the minimum concentration of SO_4^{2-} required to precipitate $BaSO_4$ in a solution containing $1.0\times10^{-4}\ mol\ Ba^{2+}$? (K_{sp} for $BaSO_4$ is 4×10^{-10}) **[MP PMT 2000]**

(a) $4\times10^{-10}M$ (b) $2\times10^{-7}M$

(c) $4\times10^{-6}M$ (d) $2\times10^{-3}M$

82. Solubility product for salt AB_2 is 4×10^{-12}. Calculate solubility **[RPET 2003]**

(a) $1\times10^{-3}\ gm\,mol/litre$

(b) $1\times10^{-5}\ gm\,mol/litre$

(c) $1\times10^{-4}\ gm\,mol/litre$

(d) $1\times10^{-2}\ gm\,mol/litre$

83. Solubility product of a salt *AB* is 1×10^{-8} in a solution in which concentration of *A* is $10^{-3}M$. The salt will precipitate when the concentration of *B* becomes more than **[MP PET 1990; KCET 2003]**

(a) $10^{-4}M$ (b) $10^{-7}M$

(c) $10^{-6}M$ (d) $10^{-5}M$

84. At equilibrium, if to a saturated solution of $NaCl, HCl$ is passed, $NaCl$ gets precipitated because **[RPMT 1999]**

(a) HCl is a strong acid
(b) Solubility of $NaCl$ decreases
(c) Ionic product of $NaCl$ becomes greater than its K_{sp}
(d) HCl is a weak acid

85. The solubility product of $BaSO_4$ is 1.3×10^{-9}. The solubility of this salt in pure water will be **[MP PET 2002]**

(a) $1.69\times10^{-9} mol\,litre^{-1}$ (b) $1.69\times10^{-18} mol\,litre^{-1}$
(c) $3.6\times10^{-18} mol\,litre^{-1}$ (d) $3.6\times10^{-5} mol\,litre^{-1}$

86. The solubility product of $AgCl$ under standard conditions of temperature is given by **[Kerala (Med.) 2003]**

(a) 1.6×10^{-5} (b) 1.5×10^{-8}
(c) 3.2×10^{-10} (d) 1.5×10^{-10}

87. An aqueous solution of CH_3COONa will be **[MP PET 2001]**

(a) Acidic (b) Alkaline
(c) Neutral (d) None of these

88. In which of the following salt hydrolysis takes place **[CPMT 1974, 78]**

(a) KCl (b) $NaNO_3$
(c) CH_3COOK (d) K_2SO_4

89. At 90^oC pure water has $[H_3O^+]=10^{-6} M$, the value of K_w at this temperature will be
[IIT 1981; MNR 1990; CBSE PMT 1993; UPSEAT 1999]

(a) 10^{-6} (b) 10^{-12}
(c) 10^{-14} (d) 10^{-8}

90. Solubility of MX_2 type electrolyte is $0.5\times10^{-4} mole/litre$. The value of K_{sp} of the electrolyte is **[CBSE PMT 2002]**

(a) 5×10^{-13} (b) 25×10^{-10}
(c) 1.25×10^{-13} (d) 5×10^{12}

91. According to the reaction $PbCl_2 = Pb^2 + 2Cl^-$, the solubility coefficient of $PbCl_2$ is **[MP PET/PMT 1988]**

(a) $[Pb^{2+}][Cl^-]^2$ (b) $[Pb^{2+}][Cl^-]$
(c) $[Pb^{2+}]^2[Cl^-]$ (d) None of these

92. K_{sp} value of $Al(OH)_3$ and $Zn(OH)_2$ are 8.5×10^{-23} and 1.8×10^{-14} respectively. If NH_4OH is added in a solution of Al^{3+} and Zn^{2+}, which will precipitate earlier **[MP PMT 1989; CPMT 1989]**

(a) $Al(OH)_3$ (b) $Zn(OH)_2$
(c) Both together (d) None

93. Why pure $NaCl$ is precipitated when HCl gas is passed in a saturated solution of $NaCl$
[NCERT 1977; MP PMT 1987; CPMT 1974, 78, 81]

(a) Impurities dissolves in HCl
(b) The value of $[Na^+]$ and $[Cl^-]$ becomes smaller than K_{sp} of $NaCl$
(c) The value of $[Na^+]$ and $[Cl^-]$ becomes greater than K_{sp} of $NaCl$
(d) HCl dissolves in the water

94. Pure $NaCl$ is prepared by saturating a cold saturated solution of common salt in water with HCl gas. The principle used is **[AFMC 1992]**

(a) Le Chatelier principle (b) Displacement law
(c) Common ion effect (d) Fractional distillation

95. What is the solubility of calcium fluoride in a saturated solution, if its solubility product is 3.2×10^{-11} **[CPMT 1997]**

(a) $2.0\times10^{-4} mole/litre$ (b) $12.0\times10^{-3} mole/litre$
(c) $0.2\times10^{-4} mole/litre$ (d) $2\times10^{-3} mole/litre$

96. The following equilibrium exists in an aqueous solution of hydrogen sulphide :

$H_2S \rightleftarrows H^+ + HS^-$

If dilute HCl is added to an aqueous solution of H_2S without any change in temperature **[NCERT 1989]**

(a) The equilibrium constant will change
(b) The concentration of HS^- will increase
(c) The concentration of undissociated H_2S will decrease
(d) The concentration of HS^- will decrease

97. Solubility of a salt M_2X_3 is $y\ mol dm^{-3}$. The solubility product of the salt will be
[IIT 1990, 97; AFMC 1991; RPMT 1999; MP PET 2001; MP PMT 2003; Orissa JEE 2005]

(a) $6y^4$ (b) $64y^4$
(c) $36y^5$ (d) $108y^5$

98. Which one of the following is most soluble **[CBSE PMT 1994; RPMT 2000]**

(a) $CuS(K_{sp}=8\times10^{-37})$ (b) $MnS(K_{sp}=7\times10^{-16})$
(c) $Bi_2S_3(K_{sp}=1\times10^{-70})$ (d) $Ag_2S(K_{sp}=6\times10^{-51})$

99. The solubility product of $PbCl_2$ at 20^oC is 1.5×10^{-4}. Calculate the solubility **[Bihar CEE 1995; BHU 2002]**

(a) 3.75×10^{-4} (b) 3.34×10^{-2}
(c) 3.34×10^{2} (d) None of these

100. Which one of the following compounds is a Lewis acid **[EAMCET 1997]**
(a) PCl_3 (b) BCl_3
(c) NCl_3 (d) $CHCl_3$

101. Which one of the following salt is most acidic in water **[IIT 1995]**
(a) $NiCl_2$ (b) $BeCl_2$
(c) $FeCl_3$ (d) $AlCl_3$

102. Which of the following aqueous solution will have a pH less than 7.0 **[MP PMT 1991, 92]**
(a) KNO_3 (b) $NaOH$
(c) $FeCl_3$ (d) $NaCN$

103. Hydrolysis constant for a salt of weak acid and weak base would be **[RPMT 1999]**
(a) $K_h=\frac{K_w}{K_a}$ (b) $K_h=\frac{K_w}{K_b}$
(c) $K_h=\frac{K_w}{K_aK_b}$ (d) None of these

104. Which salt will give basic solution on hydrolysis **[RPMT 1997]**
(a) KCN (b) KCl
(c) NH_4Cl (d) CH_3COONH_4

105. Which of the following sulphides has the lowest solubility product **[KCET 1996]**
(a) FeS (b) MnS
(c) PbS (d) ZnS

106. The concentration of which ion is to be decreased, when NH_3 solution is added **[RPMT 1997]**
(a) OH^- (b) NH_4^+
(c) H_3O^+ (d) O_2^-

107. The compound insoluble in acetic acid is **[IIT 1986]**
(a) Calcium oxide
(b) Calcium carbonate
(c) Calcium oxalate
(d) Calcium hydroxide

108. A saturated solution of Ag_2SO_4 is $2.5\times10^{-2}\,M$; The value of its solubility product is **[Pb.CET 2004]**
(a) 62.5×10^{-6} (b) 6.25×10^{-4}
(c) 15.625×10^{-6} (d) 3.125×10^{-6}

109. Solubility product of $AgCl$ is 1×10^{-6} at 298 K. Its solubility in mole $litre^{-1}$ would be **[Pb.CET 2001]**
(a) $1\times10^{-6}\,mol/litre$
(b) $1\times10^{-3}\,mol/litre$
(c) $1\times10^{-12}\,mol/litre$
(d) None of these

110. A litre of solution is saturated with $AgCl$. To this solution if 1.0×10^{-4} mole of solid $NaCl$ is added, what will be the $[Ag^+]$, assuming no volume change **[UPSEAT 2004]**
(a) More (b) Less
(c) Equal (d) Zero

111. The concentration of KI and KCl in certain solution containing both is 0.001M each. If 20 ml of this solution is added to 20 ml of a saturated solution of AgI in water? What will happen **[MP PMT 2004]**
(a) $AgCl$ will be precipitated
(b) AgI will be precipitated
(c) Both $AgCl$ and AgI will be precipitated
(d) There will be no precipitated

112. The solubility product of a sparingly soluble salt AX_2 is 3.2×10^{-11}. Its solubility (in moles / litres) is **[CBSE PMT 2004]**
(a) 2×10^{-4} (b) 4×10^{-4}
(c) 5.6×10^{-6} (d) 3.1×10^{-4}

113. 0.5 M ammonium benzoate is hydrolysed to 0.25 percent, hence its hydrolysis constant is **[MH CET 2004]**
(a) 2.5×10^{-5} (b) 1.5×10^{-4}
(c) 3.125×10^{-6} (d) 6.25×10^{-4}

114. The solubility of Sb_2S_3 in water is 1.0×10^{-5} mol / litre at 298 K. What will be its solubility product **[CPMT 2004]**
(a) 108×10^{-25} (b) 1.0×10^{-25}
(c) 144×10^{-25} (d) 126×10^{-24}

115. The ionic product of water at 25^oC is 10^{-14}. The ionic product at 90^oC will be **[CBSE PMT 1996]**
(a) 1×10^{-20} (b) 1×10^{-12}
(c) 1×10^{-14} (d) 1×10^{-16}

116. In hydrolysis of a salt of weak acid and strong base, $A^- + H_2O \rightleftarrows HA + OH^-$, the hydrolysis constant (K_h) is equal to…. **[Orissa JEE 2002]**
(a) $\frac{K_w}{K_a}$ (b) $\frac{K_w}{K_b}$
(c) $\sqrt{\frac{K_a}{C}}$ (d) $\frac{K_w}{K_a\times K_b}$

Hydrogen ion concentration- *p*H scale and Buffer solution

1. The pH of blood does not appreciably change by a small addition of an acid or a base because blood **[CBSE PMT 1995]**

(a) Contains serum protein which acts as buffer
(b) Contains iron as a part of the molecule
(c) Can be easily coagulated
(d) It is body fluid

2. The pH of a $0.001 M\ NaOH$ will be **[MP PMT 1995; UPSEAT 2001]**

(a) 3 (b) 2
(c) 11 (d) 12

3. *pH* value of a solution, whose hydronium ion concentration is $6.2 \times 10^{-9} mol/l$, is **[AFMC 1999; AIIMS 2000]**

(a) 6.21 (b) 7.21
(c) 7.75 (d) 8.21

4. 0.1 mole of CH_3NH_2 ($K_b = 5 \times 10^{-4}$) is mixed with 0.08 mole of *HCl* and diluted to one litre. What will be the H^+ concentration in the solution? **[IIT 2005]**

(a) 8×10^{-2} *M* (b) 8×10^{-11} *M*
(c) 1.6×10^{-11} *M* (d) 8×10^{-5} *M*

5. What will be the sum of pH and pOH in an aqueous solution ? **[MP PET/PMT 1998]**

(a) 7 (b) pk_w
(c) Zero (d) 1

6. Hydrogen ion concentration in *mol/L* in a solution of $pH = 5.4$ will be **[AIEEE 2005]**

(a) 3.98×10^8 (b) 3.88×10^6
(c) 3.68×10^{-6} (d) 3.98×10^{-6}

7. When solid potassium cyanide is added in water then **[CPMT 2002; BHU 2002]**

(a) *pH* will increase
(b) *pH* will decrease
(c) *pH* will remain the same
(d) Electrical conductivity will not change

8. *pH* of a $10^{-3} M$ solution of hydrochloric acid will be **[MP PET 2000]**

(a) 1.3 (b) 2.0
(c) 3.0 (d) 4.5

9. The pH of water at 25^0C is nearly **[CPMT 1986, 89, 90, 93; CBSE PMT 1989; MADT Bihar 1995]**

(a) 2 (b) 7
(c) 10 (d) 12

10. pH of a solution is 5. Its hydroxyl ion concentration is **[JIPMER 1999]**

(a) 5 (b) 10
(c) 10^{-5} (d) 10^{-9}

11. The pH of a solution in which the $[H^+] = 0.01$, is **[MADT Bihar 1980]**

(a) 2 (b) 1
(c) 4 (d) 3

12. At 25°*C*, the dissociation constant of a base *BOH* is 1.0×10^{-12}. The concentration of Hydroxyl ions in 0.01 *M* aqueous solution of the base would be **[CBSE PMT 2005]**

(a) $2.0 \times 10^{-6} mol L^{-1}$ (b) $1.0 \times 10^{-5} mol L^{-1}$
(c) $1.0 \times 10^{-6} mol L^{-1}$ (d) $1.0 \times 10^{-7} mol L^{-1}$

13. Aqueous solution of HCl has the $pH = 4$. Its molarity would be **[RPMT 1999]**

(a) 4 *M* (b) 0.4 *M*
(c) 0.0001 *M* (d) 10 *M*

14. Which is a buffer solution **[CPMT 1985, 88; AIIMS 1980; MP PMT 1994; AFMC 2004]**

(a) $CH_3COOH + CH_3COONa$
(b) $CH_3COOH + CH_3COONH_4$
(c) $CH_3COOH + NH_4Cl$
(d) $NaOH + NaCl$

15. The addition of solid sodium carbonate to pure water causes **[NCERT 1973]**

(a) An increase in hydronium ion concentration
(b) An increase in alkalinity
(c) No change in acidity
(d) A decrease in hydroxide ion concentration

16. The aqueous solution of which of the following salt has the lowest *pH* **[CBSE PMT 2002]**

(a) $NaClO$ (b) $NaClO_2$
(c) $NaClO_3$ (d) $NaClO_4$

17. The pH of a $10^{-10} M\ NaOH$ solution is nearest to **[UPSEAT 2001, 02]**

(a) 10 (b) 7
(c) 4 (d) -10

18. Which will have maximum pH **[NCERT 1979]**

(a) Distilled water
(b) $1M\ NH_3$
(c) $1M\ NaOH$
(d) Water saturated by chlorine

19. *pH* of a solution is 9.5. The solution is **[MH CET 2000]**

(a) Neutral (b) Acidic
(c) Basic (d) Amphoteric

20. The pH of a $10^{-9}M$ solution of HCl in water is **[UPSEAT 2000, 02]**

(a) 8 (b) – 8

(c) Between 7 and 8 (d) Between 6 and 7

21. $pH + pOH$ equal to **[NCERT 1975]**

(a) Zero (b) Fourteen

(c) A negative number (d) Infinity

22. Which of the following 0.1*M* solution will contain the largest concentration of hydronium ions **[NCERT 1971, 73]**

(a) $NaHCO_3$ (b) NH_4Cl

(c) HCl (d) NH_3

23. Which one has pH 12 **[Roorkee 1995]**

(a) $0.01M\ KOH$ (b) $1N\ KOH\ ml$

(c) $1N\ NaOH\ ml$ (d) $1N\ Ca(OH)_2\ ml$

24. What is the correct relationship between the pHs of isomolar solutions of sodium oxide (pH_1), sodium sulphide (pH_2), sodium selenide (pH_3) and sodium telluride (pH_4)? **[CBSE PMT 2005]**

(a) $pH_1 > pH_2 = pH_3 > pH_4$

(b) $pH_1 < pH_2 < pH_3 < pH_4$

(c) $pH_1 < pH_2 < pH_3 = pH_4$

(d) $pH_1 > pH_2 > pH_3 > pH_4$

25. Given *pH* of a solution *A* is 3 and it is mixed with another solution *B* having *pH* 2. If both mixed then resultant *pH* of the solution will be **[BHU 2005]**

(a) 3.2 (b) 1.9

(c) 3.4 (d) 3.5

26. On adding solid potassium cyanide to water **[MP PMT 1989]**

(a) *pH* will increase

(b) *pH* will decrease

(c) *pH* will not change

(d) Electrical conductance will not change

27. *A* is an aqueous acid; *B* is an aqueous base. They are diluted separately, then **[KCET 2002]**

(a) pH of *A* increases and pH of *B* decreases

(b) pH of *A* increases and pH of *B* decreases till pH in each case is 7

(c) pH of *A* and *B* increase

(d) pH of *B* and *A* decrease

28. The compound whose 0.1 *M* solution is basic is **[IIT 1986; MP PMT 1991]**

(a) Ammonium acetate

(b) Calcium carbonate

(c) Ammonium sulphate

(d) Sodium acetate

29. The following reaction is known to occur in the body $CO_2 + H_2O \rightleftharpoons H_2CO_3 \rightleftharpoons H^+ + HCO_3^-$. If CO_2 escapes from the system **[NCERT 1973; RPMT 1997]**

(a) pH will decrease

(b) Hydrogen ion concentration will decrease

(c) H_2CO_3 concentration will be unaltered

(d) The forward reaction will be promoted

30. For preparing a buffer solution of pH 6 by mixing sodium acetate and acetic acid, the ratio of the concentration of salt and acid should be $(K_a = 10^{-5})$ **[MP PET 1997]**

(a) $1:10$ (b) $10:1$

(c) $100:1$ (d) $1:100$

31. Which is incorrect for buffer solution **[CPMT 1985]**

(a) It contains weak acid and its conjugate base

(b) It contains weak base and its conjugate acid

(c) In this there is very less change is pH value when very less amount of acid and base is mixed

(d) None of the above

32. pH values of HCl and $NaOH$ solutions each of strength $\frac{N}{100}$ will be respectively **[MP PMT 1999]**

(a) 2 and 2 (b) 2 and 12

(c) 12 and 2 (d) 2 and 10

33. When rain is accompained by a thunderstorm, the collected rain water will have a *pH* value **[AIEEE 2003]**

(a) Slightly lower than that of rain water without thunderstorm

(b) Slightly higher than that when the thunderstorm is not there

(c) Uninfluenced by occurrence of thunderstorm

(d) Which depends on the amount of dust in air

34. Which of the following is the buffer solution of strong acidic nature **[MP PET 2002]**

(a) $HCOOH + HCOO^-$

(b) $CH_3COOH + CH_3COO^-$

(c) $H_2C_2O_4 + C_2O_4^{2-}$

(d) $H_3BO_3 + BO_3^{3-}$

35. The dissociation constant of an acid *HA* is 1×10^{-5}. The pH of 0.1 molar solution of the acid will be **[KCET (Engg./Med.) 1999]**

(a) Five (b) Four

(c) Three (d) One

36. The *pH* value of $1.0\times10^{-8}M\ HCl$ solution is less than 8 because

(a) HCl is completely ionised at this concentration

(b) The ionization of water is negligible

(c) The ionization of water cannot be assumed to be negligible in comparison with this low concentration of HCl

(d) The *pH* cannot be calculated at such a low concentration of HCl

37. What is the *pH* for a neutral solutions at the normal temperature of the human body **[JIPMER 2000]**

(a) 7.2 (b) 14.0
(c) 6.8 (d) 6.0

38. 1 *M* $NaCl$ and 1 *M* HCl are present in an aqueous solution. The solution is **[AIEEE 2002]**

(a) Not a buffer solution with *pH* < 7
(b) Not a buffer solution with *pH* > 7
(c) A buffer solution with *pH* < 7
(d) A buffer solution with *pH* > 7

39. A solution has $pH = 5$, it is diluted 100 times, then it will become **[NCERT 1978; AFMC 2005]**

(a) Neutral (b) Basic
(c) Unaffected (d) More acidic

40. 0.02 *M* monobasic acid dissociates 2% hence, pH of the solution is **[MH CET 2000]**

(a) 0.3979 (b) 1.3979
(c) 1.699 (d) 3.3979

41. Components of buffer solution are $0.1M\ HCN$ and $0.2M\ NaCN$. What is the *pH* of the solution **[RPET 2000]**

(a) 9.61 (b) 6.15
(c) 2.0 (d) 4.2

42. *pH* of a solution of $10ml$. 1*N* sodium acetate and $50ml$ 2*N* acetic acid $(K_a = 1.8 \times 10^{-5})$, is approximately

[MP PMT 2003]

(a) 4 (b) 5
(c) 6 (d) 7

43. By adding $20ml$ $0.1N\ HCl$ to $20ml$ $0.001N$ KOH, the *pH* of the obtained solution will be **[KCET 2000]**

(a) 2 (b) 1.3
(c) 0 (d) 7

44. The *pH* of the solution containing $10ml$ of a $0.1N\ NaOH$ and $10ml$ of $0.05N$ H_2SO_4 would be

[Pb. PMT 2002, 04]

(a) 1 (b) 0
(c) 7 (d) > 7

45. The pH of $10^{-7}M\ NaOH$ is **[MP PMT 2001]**

(a) 7.01 (b) Between 7 and 8
(c) Between 9 and 10 (d) Greater than 10

46. The hydrogen ion concentration of $0.1N$ solution of CH_3COOH, which is 30% dissociated, is **[JIPMER 2002]**

(a) 0.03 (b) 3.0
(c) 0.3 (d) 30.0

47. What is the *pH* of $0.1M\ NH_3$ **[RPET 2000]**

(a) 11.27 (b) 11.13
(c) 12.0 (d) 9.13

48. By adding a strong acid to the buffer solution, the *pH* of the buffer solution **[DPMT 1996]**

(a) Remains constant (b) Increases
(c) Decreases (d) Becomes zero

49. The *pH* of $0.1M\ NaOH$ is **[MP PET 2003]**

(a) 11 (b) 12
(c) 13 (d) 14

50. *pH* of human blood is 7.4. Then H^+ concentration will be

[RPMT 2002]

(a) 4×10^{-8} (b) 2×10^{-8}
(c) 4×10^{-4} (d) 2×10^{-4}

51. Assuming complete ionisation, the *pH* of $0.1M\ HCl$, is 1. The molarity of H_2SO_4 with the same *pH* is

[Pb. PMT 2002]

(a) 0.1 (b) 0.2
(c) 0.05 (d) 2.0

52. Highest *pH* 14 is given by **[DCE 1999]**

(a) $0.1M\ H_2SO_4$ (b) $0.1M\ NaOH$
(c) $1N\ NaOH$ (d) $1N\ HCl$

53. What will be the pH of a $10^{-8}\ M\ HCl$ solution

[MP PET/PMT 1998; RPET 1999;MP PMT 2000]

(a) 8.0 (b) 7.0
(c) 6.98 (d) 14.0

54. When 10 *ml* of 0.1 *M* acetic acid $(pK_a = 5.0)$ is titrated against 10 *ml* of 0.1*M* ammonia solution $(pK_b = 5.0)$, the equivalence point occurs at *pH* **[AIIMS 2005]**

(a) 5.0 (b) 6.0
(c) 7.0 (d) 9.0

55. Which on reaction with water will have pH less than 7

[MH CET 2001]

(a) BaO (b) CaO
(c) Na_2O (d) P_2O_5

56. A solution of $MgCl_2$ in water has *pH*

[MP PMT 2002]

(a) < 7 (b) > 7
(c) 7 (d) 14.2

57. *pH* of completely dissociated $0.005M\ H_2SO_4$ is

[RPET 2003]

(a) 3 (b) 4
(c) 2 (d) 5

58. The pK_a of a weak acid is 4.8. What should be the ratio of [Acid]/[Salt] of a buffer if $pH = 5.8$ is required

[MP PET 2003]

(a) 10 (b) 0.1

(c) 1 (d) 2

59. Which of the following salt is acidic **[CPMT 1979, 81; NCERT 1979, 81; MP PET 1990; JIPMER 2002]**

(a) Na_2SO_4 (b) $NaHSO_3$

(c) Na_2SO_3 (d) Na_2S

60. $20 ml$ of $0.5 N\ HCl$ and $35 ml$ of $0.1 N\ NaOH$ are mixed. The resulting solution will **[KCET 2005]**

(a) Be neutral

(b) Be basic

(c) Turn phenolphthalein solution pink

(d) Turn methyl orange red

61. The pH of a 0.02 *M* solution of hydrochloric acid is **[MP PMT 1993]**

(a) 2.0 (b) 1.7

(c) 0.3 (d) 2.2

62. A sample of $Na_2CO_3.H_2O$ weighing $0.62\ g$ is added to $100 ml$ of $0.1 N\ (NH_4)_2SO_4$ solution. What will be the resulting solution **[BHU 1997]**

(a) Acidic (b) Neutral

(c) Basic (d) None of these

63. The *pH* of the solution is 4. The hydrogen ion concentration of the solution in *mol/litre* is **[UPSEAT 2000]**

(a) 9.5 (b) 10^{-4}

(c) 10^4 (d) 10^{-2}

64. $NaOH_{(aq)}, HCl_{(aq)}$ and $NaCl_{(aq)}$ concentration of each is $10^{-3} M$. Their *pH* will be respectively **[BHU 2003]**

(a) 10, 6, 2 (b) 11, 3, 7

(c) 10, 2, 6 (d) 3, 4, 7

65. The pH of $10^{-5} M$ aqueous solution of $NaOH$ is **[MP PET 1996]**

(a) 5 (b) 7

(c) 9 (d) 11

66. The pH of 0.05 *M* solution of dibasic acid is **[MH CET 2002]**

(a) $+1$ (b) -1

(c) $+2$ (d) -2

67. A buffer solution contains $0.1\ M$ of acetic acid and $0.1\ M$ of sodium acetate. What will be its pH, if pK_a of acetic acid is 4.75 **[MP PMT 1996]**

(a) 4.00 (b) 4.75

(c) 5.00 (d) 5.25

68. To obtain a buffer which should be suitable for maintaining a pH of about $4-5$, we need to have in solution, a mixture of

(a) A strong base + its salt with a weak acid

(b) A weak base + its salt with a strong acid

(c) A strong acid + its salt with a weak base

(d) A weak acid + its salt with a strong base

69. The concentration of $NaOH$ solution is $10^{-8} M$. Find out the (OH^-) concentration **[CPMT 1993]**

(a) 10^{-8}

(b) Greater than 10^{-6}

(c) 10^{-6}

(d) Lies between 10^{-6} and 10^{-7}

70. The pH of $0.0001 N$ solution of KOH will be **[BHU 1997; CET Pune 1998]**

(a) 4 (b) 6

(c) 10 (d) 12

71. Given that the dissociation constant for H_2O is $K_w = 1 \times 10^{-14}\ mole^2\ litre^{-2}$, what is the pH of a $0.001 molar KOH$ solution **[MP PET 1995; MP PET/PMT 1998]**

(a) 10^{-11} (b) 3

(c) 14 (d) 11

72. An acidic buffer solution can be prepared by mixing solution of **[MNR 1983]**

(a) Ammonium acetate and acetic acid

(b) Ammonium chloride and hydrochloric acid

(c) Sulphuric acid and sodium sulphate

(d) Acetic acid and sulphuric acid

(e) $NaCl$ and $NaOH$

73. Which of the following mixtures forms an acid buffer **[MP PMT 1993; IIT 1981; CPMT 1989; CBSE PMT 1989]**

(a) $NaOH + HCl$

(b) $CH_3COOH + CH_3COONa$

(c) $NH_4OH + NH_4Cl$

(d) $H_2CO_3 + (NH_4)_2CO_3$

74. A buffer solution has equal volumes of $0.2 M\ NH_4OH$ and $0.02 M\ NH_4Cl$. The pK_b of the base is 5. The *pH* is **[CBSE PMT 1989; KCET 2005]**

(a) 10 (b) 9

(c) 4 (d) 7

75. The pH of a simple sodium acetate buffer is given by $pH = pK_a + \log\frac{[Salt]}{[Acid]}$

K_a of acetic acid $= 1.8 \times 10^{-5}$

If [Salt] = [Acid] = 0.1 *M*, the pH of the solution would be about **[BHU 1987]**

(a) 7 (b) 4.7

(c) 5.3 (d) 1.4

76. Amongst the following solutions, the buffer solution is **[MP PMT 1999]**

(a) $NH_4Cl + NH_4OH$ solution

(b) $NH_4Cl + NaOH$ solution

(c) $NH_4OH + HCl$ solution

(d) $NaOH + HCl$ solution

77. The pH of solution having $[OH^-] = 10^{-7}$ is **[AIIMS 1996]**

(a) 7 (b) 14

(c) Zero (d) - 7

78. $50\,ml$ water is added to a $50\,ml$ solution of $Ba(OH)_2$ of strength $0.01\,M$. The pH value of the resulting solution will be **[MP PMT 1999]**

(a) 8 (b) 10

(c) 12 (d) 6

79. pH of a solution can be expressed as **[CPMT 1999; UPSEAT 2001]**

(a) $-\log_e(H^+)$ (b) $-\log_{10}(H^+)$

(c) $\log_e(H^+)$ (d) $\log_{10}(H^+)$

80. The solution of sodium carbonate has *pH* **[MP PET 2000]**

(a) Greater than 7 (b) Less than 7

(c) Equal to 7 (d) Equal to zero

81. The pH of $10^{-7}\,N\,HCl$ is **[RPMT 2000]**

(a) 6.0 (b) 6.97

(c) 8.0 (d) 10.0

82. If the pH of a solution is 2, its normality will be **[MADT Bihar 1982; MP PET 2000]**

(a) 2*N* (b) $\frac{1}{2}N$

(c) 0.01 *N* (d) None of these

83. The buffer solution of 100 ml having a pH value 4 when added to 1 ml dilute HCl, then the pH of buffer solution **[NCERT 1976, 77]**

(a) Converts to 7 (b) Does not change

(c) Converts to 2 (d) Changes to 10

84. In a solution of acetic acid, sodium acetate is added, then its pH value **[NCERT 1977; DPMT 1985; MP PMT 1994]**

(a) Decreases

(b) Increases

(c) Remains unchanged

(d) (a) and (b) both are correct

85. If *pOH* of a solution is 6.0, then its *pH* will be **[MP PMT 1987]**

(a) 6 (b) 10

(c) 8 (d) 14

86. In a solution of $pH = 5$, more acid is added in order to reduce the $pH = 2$. The increase in hydrogen ion concentration is **[MP PET 1989; CPMT 1990]**

(a) 100 times (b) 1000 times

(c) 3 times (d) 5 times

87. Which solution contains maximum number of H^+ ion

(a) 0.1 M HCl (b) 0.1 M NH_4Cl

(c) 0.1 M $NaHCO_3$ (d) 0.1 M

88. A certain buffer solution contains equal concentration of X^- and HX. The K_b for X^- is 10^{-10}. The pH of the buffer is **[IIT 1984; RPMT 1997; CPMT 1996; DPMT 2004]**

(a) 4 (b) 7

(c) 10 (d) 14

89. The defination of pH is **[EAMCET 1980; UPSEAT 2001]**

(a) $pH = \log\frac{1}{[H^+]}$ (b) $pH = \log[H^+]$

(c) $pH = -\log\frac{1}{[H^+]}$ (d) $pH = -\log^{[H^+]}$

90. Which of the following does not make any change in pH when added to $10\,ml$ dilute HCl **[NCERT 1975]**

(a) 5 *ml* pure water (b) 20 *ml* pure water

(c) 10 $ml\ HCl$ (d) Same 20 ml dilute HCl

91. A compound whose aqueous solution will have the highest pH **[CPMT 1974, 75, 78; MP PET 1996; DPMT 1982, 83]**

(a) $NaCl$ (b) Na_2CO_3

(c) NH_4Cl (d) $NaHCO_3$

92. At $80^\circ C$, distilled water has $[H_3O^+]$ concentration equal to 1×10^{-6} $mole/litre$ The value of K_w at this temperature will be **[CBSE PMT 1994; RPMT 2000; AFMC 2001; AIIMS 2002; BHU 2002]**

(a) 1×10^{-6} (b) 1×10^{-9}

(c) 1×10^{-12} (d) 1×10^{-15}

93. The pH value of $0.1\,M\ NaOH$ solution is (when there is a given reaction $[H^+][OH^-] = 10^{-15}$) **[CPMT 1997]**

(a) 13 (b) 12

(c) 11 (d) 2

94. Which oxychloride has maximum pH **[CPMT 1997]**

(a) $NaClO$ (b) $NaClO_2$

(c) $NaClO_3$ (d) $NaClO_4$

95. pH of $HCl\,(10^{-12}M)$ is **[CPMT 1997; Pb. PET/PMT 1999]**

(a) 12 (b) -12

(c) ≈ 7 (d) 14

96. Which one is buffer solution **[CPMT 1997]**

(a) $[PO_4^{---}][[HPO_4^{---}]$ (b) $[PO_3^{3-}][[H_2PO_4^{---}]$

(c) $[HPO_4^{---}][[H_2PO_4^{---}]$ (d) All of these

97. When $100\,ml$ of $M/10\,NaOH$ solution and $50\,ml$ of $M/5\,HCl$ solution are mixed, the pH of resulting solution would be **[RPMT 1997]**

(a) 0 (b) 7

(c) Less than 7 (d) More than 7

98. How many millilitres of $6.0\,M$ hydrochloric acid should be used to prepare $150\,ml$ of a solution which is $0.30\,M$ in hydrogen ion **[Pb. PMT 1998]**

(a) 3.0 (b) 7.5

(c) 9.3 (d) 30

99. The *pH* of 0.1 *M* acetic acid is 3, the dissociation constant of acid will be

(a) 1.0×10^{-4} (b) 1.0×10^{-5}

(c) 1.0×10^{-3} (d) 1.0×10^{-8}

100. The pH of a buffer solution containing $25\,ml$ of $1\,M\,CH_3COONa$ and $25\,ml$ of $1\,M\,CH_3COOH$ will be appreciably affected by $5\,ml$ of **[CPMT 1987]**

(a) $1\,M\,CH_3COOH$ (b) $5\,M\,CH_3COOH$

(c) $5\,M\,HCl$ (d) $1\,M\,NH_4OH$

101. The pH value of decinormal solution of NH_4OH which is 20% ionised, is **[CBSE PMT 1998]**

(a) 13.30 (b) 14.70

(c) 12.30 (d) 12.95

102. A physician wishes to prepare a buffer solution at $pH=3.58$ that efficiently resists changes in pH yet contains only small concentration of the buffering agents. Which of the following weak acids together with its sodium salt would be best to use **[CBSE PMT 1997]**

(a) m- chlorobenzoic acid $(pK_a=3.98)$

(b) p- chlorocinnamic acid $(pK_a=4.41)$

(c) $2,5$- dihydroxy benzoic acid $(pK_a=2.97)$

(d) Acetoacetic acid $(pK_a=3.58)$

103. In a mixture of a weak acid and its salt, the ratio of concentration of acid to salt is increased ten-fold. The pH of the solution **[KCET 1996]**

(a) Decreases by one (b) Increases by one-tenth

(c) Increases by one (d) Increases ten-fold

104. When an acid or alkali is mixed with buffer solution, then pH of buffer solution **[CPMT 1997]**

(a) Not changes (b) Changes slightly

(c) Increases (d) Decreases

105. How much sodium acetate should be added to a $0.1\,m$ solution of CH_3COOH to give a solution of $pH=5.5\,(pK_a$ of $CH_3COOH=4.5)$ **[KCET 1996]**

(a) $0.1\,m$ (b) $0.2\,m$

(c) $1.0\,m$ (d) $10.0\,m$

106. The pH of the aqueous solution containing $0.49\,gm$ of H_2SO_4 in one litre is **[EAMCET 1997]**

(a) 2 (b) 1

(c) 1.7 (d) 0.3

107. Which of the following solutions can act as buffer **[JIPMER 1997]**

(a) 0.1 molar aq. $NaCl$

(b) 0.1 molar aq. $CH_3COOH+0.1$ molar $NaOH$

(c) 0.1 molar aq. ammonium acetate

(d) None of the above

108. The pH of a solution obtained by mixing $50\,ml$ of $0.4\,N\,HCl$ and $50\,ml$ of $0.2\,N\,NaOH$ is **[KCET 1996]**

(a) $-\log 2$ (b) $-\log 0.2$

(c) 1.0 (d) 2.0

109. Which of the following is a buffer **[MP PMT 1991; BHU 1995]**

(a) $NaOH+CH_3COONa$

(b) $NaOH+Na_2SO_4$

(c) $K_2SO_4+H_2SO_4$

(d) $NH_4OH+CH_3COONH_4$

110. If 4.0 *gm* $NaOH$ is present in 1 *litre* solution, then its pH will be **[CPMT 1989]**

(a) 6 (b) 13

(c) 18 (d) 24

111. The pOH of beer is 10.0. The hydrogen ion concentration will be **[MP PMT 1994]**

(a) 10^{-2} (b) 10^{-10}

(c) 10^{-8} (d) 10^{-4}

112. When a buffer solution of sodium acetate and acetic acid is diluted with water **[CPMT 1985]**

(a) Acetate ion concentration increases

(b) H^+ ion concentration increases

(c) OH^- ion concentration increases

(d) H^+ ion concentration remain unaltered

113. What is the pH of $Ba(OH)_2$ if normality is 10 **[CPMT 1996]**

(a) 4 (b) 10

(c) 7 (d) 9

114. What will be the pH of a solution formed by mixing $40\,ml$ of $0.10\,M\,HCl$ with $10\,ml$ of $0.45\,M\,NaOH$ **[Manipal MEE 1995]**

(a) 12 (b) 10
(c) 8 (d) 6

115. The pH of a solution having $[H^+] = 10 \times 10^{-4}$ $moles/litre$ will be **[BHU 1981]**
(a) 1 (b) 2
(c) 3 (d) 4

116. If $0.4\, gm\, NaOH$ is present in 1 *litre* solution, then its pH will be **[CPMT 1985; BHU 1980]**
(a) 2 (b) 10
(c) 11 (d) 12

117. Which of the following is not a Bronsted acid **[BHU 1997]**
(a) $CH_3NH_4^+$ (b) CH_3COO^-
(c) H_2O (d) HSO_4^-

118. pH of 0.005 M H_2SO_4 solution will be **[NCERT 1980]**
(a) 0.005 (b) 2
(c) 1 (d) 0.01

119. A buffer solution is a mixture of **[MP PMT 1987]**
(a) Strong acid and strong base
(b) Weak acid and weak base
(c) Weak acid and conjugate acid
(d) Weak acid and conjugate base

120. When pH of a solution decreases, its hydrogen ion concentration **[MADT Bihar 1981]**
(a) Decreases (b) Increases
(c) Rapidly increases (d) Remains always constant

121. If the pH of a solution is 4.0 at 25^oC, its pOH would be $(K_w = 10^{-14})$ **[MP PMT 1989]**
(a) 4.0 (b) 6.0
(c) 8.0 (d) 10.0

122. An aqueous solution whose $pH = 0$ is **[CPMT 1976; DPMT 1982]**
(a) Alkaline (b) Acidic
(c) Neutral (d) Amphoteric

123. In a solution of acid H^+ concentration is $10^{-10}M$. The *pH* of this solution will be
(a) 8 (b) 6
(c) Between 6 and 7 (d) Between 3 and 6

124. The concentration of hydronium (H_3O^+) ion in water is **[CET Pune 1998]**
(a) Zero (b) $1 \times 10^7\, gmion/litre$
(c) $1 \times 10^{-14}\, gmion/litre$ (d) $1 \times 10^{-7}\, gmion/litre$

125. A solution whose *pH* value is less than 7 will be
(a) Basic (b) Acidic
(c) Neutral (d) Buffer

126. When the pH of a solution is 2, the hydrogen ion concentration in moles per litre is **[NCERT 1973; MNR 1979]**
(a) 1×10^{-14} (b) 1×10^{-2}
(c) 1×10^{-7} (d) 1×10^{-12}

127. A base is dissolved in water yields a solution with a hydroxide ion concentration of 0.05 $mol\, litre^{-1}$. The solution is **[AFMC 1997]**
(a) Basic (b) Acid
(c) Neutral (d) Both (a) and (b)

128. The pH of a solution is increased from 3 to 6. Its H^+ ion concentration will be **[EAMCET 1998]**
(a) Reduced to half
(b) Doubled
(c) Reduced by 1000 times
(d) Increased by 1000 times

129. Pure water is kept in a vessel and it remains exposed to atmospheric CO_2 which is absorbed, then its pH will be **[MADT Bihar 1984; DPMT 2002]**
(a) Greater than 7
(b) Less than 7
(c) 7
(d) Depends on ionic product of water

130. The pH of a solution is 2. If its pH is to be raised to 4, then the $[H^+]$ of the original solution has to be **[MP PET 1994]**
(a) Doubled
(b) Halved
(c) Increased hundred times
(d) Decreased hundred times

131. Which of the following solutions cannot act as a buffer **[EAMCET 1998]**
(a) $NaH_2PO_4 + H_3PO_4$
(b) $CH_3COOH + CH_3COONa$
(c) $HCl + NH_4Cl$
(d) $H_3PO_4 + Na_2HPO_4$

132. Assuming complete ionisation, the pH of $0.1M$ HCl is 1. The molarity of H_2SO_4 with the same pH is **[KCET 1998]**
(a) 0.2 (b) 0.1
(c) 2.0 (d) 0.05

133. The pH of blood is
(a) 5.2 (b) 6.3
(c) 7.4 (d) 8.5

134. The *pH* of 10^{-8} molar aqueous solution of HCl is **[CPMT 1988; MNR 1983, 90; MP PMT 1987; IIT 1981; BHU 1995; AFMC 1998; MP PET 1989, 99; BCECE 2005]**

(a) -8
(b) 8
(c) $6 > 7$ (Between 6 and 7)
(d) $7 > 8$ (Between 7 and 8)

135. As the temperature increases, the pH of a KOH solution **[UPSEAT 2001]**

(a) Will decreases
(b) Will increases
(c) Remains constant
(d) Depends upon concentration of KOH solution

136. The hydrogen ion concentration in a given solution is 6×10^{-4}. Its pH will be **[EAMCET 1978]**

(a) 6
(b) 4
(c) 3.22
(d) 2

137. The pH of $\frac{N}{100} HCl$ would be approximately **[CPMT 1971; DPMT 1982, 83; MP PMT 1991; Bihar MEE 1996]**

(a) 1
(b) 1.5
(c) 2
(d) 2.5

138. A solution which is resistant to change of pH upon the addition of an acid or a base is known as **[BHU 1979]**

(a) A colloid
(b) A crystalloid
(c) A buffer
(d) An indicator

139. $10^{-6} M$ HCl is diluted to 100 times. Its pH is **[CPMT 1984]**

(a) 6.0
(b) 8.0
(c) 6.95
(d) 9.5

140. The pH of a 10^{-10} molar HCl solution is approximately **[NCERT 1977]**

(a) 10
(b) 7
(c) 1
(d) 14

141. The H^+ ion concentration is 1.0×10^{-6} *mole/litre* in a solution. Its *pH* value will be **[MP PMT 1985; AFMC 1982]**

(a) 12
(b) 6
(c) 18
(d) 24

142. The pH of a solution is the negative logarithm to the base 10 of its hydrogen ion concentration in **[Manipal MEE 1995]**

(a) Moles per litre
(b) Millimoles per litre
(c) Micromoles per litre
(d) Nanomoles per litre

143. When 10^{-8} mole of HCl is dissolved in one litre of water, the pH of the solution will be **[CPMT 1973, 94; DPMT 1982]**

(a) 8
(b) 7
(c) Above 8
(d) Below 7

144. The pH of the solution containing 10 ml of 0.1 *N* $NaOH$ and 10 ml of 0.05 *N* H_2SO_4 would be **[CPMT 1987; Pb. PMT 2002,04]**

(a) 0
(b) 1
(c) > 7
(d) 7

145. The pH of 0.001 molar solution of HCl will be **[MP PET 1986; MP PET/PMT 1988; CBSE PMT 1991]**

(a) 0.001
(b) 3
(c) 2
(d) 6

146. Which salt can be classified as an acid salt **[CPMT 1989]**

(a) Na_2SO_4
(b) $BiOCl$
(c) $Pb(OH)Cl$
(d) Na_2HPO_4

147. Given a 0.1*M* solution of each of the following. Which solution has the lowest pH **[MNR 1987]**

(a) $NaHSO_4$
(b) NH_4Cl
(c) HCl
(d) NH_3

148. Out of the following, which pair of solutions is not a buffer solution

(a) $NH_4Cl + NH_4OH$
(b) $NaCl + NaOH$
(c) $Na_2HPO_4 + Na_3PO_4$
(d) $CH_3COOH + CH_3COONa$

149. If the dissociation constant of an acid *HA* is 1×10^{-5}, the pH of a 0.1 molar solution of the acid will be approximately **[NCERT 1979]**

(a) Three
(b) Five
(c) One
(d) Six

150. pH value of $N/10\ NaOH$ solution is **[CBSE PMT 1996;Pb. CET 2001; Pb. PMT 2002]**

(a) 10
(b) 11
(c) 12
(d) 13

151. A solution of sodium borate has a pH of approximately **[JIPMER 2001]**

(a) < 7
(b) > 7
(c) = 7
(d) Between 4 to 5

152. If pH of A, B, C and D are 9.5, 2.5, 3.5 and 5.5 respectively, then strongest acid is **[AFMC 1995]**

(a) A
(b) C
(c) D
(d) B

153. At $25°C$ the pH value of a solution is 6. The solution is **[AFMC 2001]**

(a) Basic
(b) Acidic
(c) Neutral
(d) Both (b) and (c)

154. A certain buffer solution contains equal concentration of X^- and HX. The K_a for *HX* is 10^{-8}. The pH of the buffer is **[UPSEAT 2001]**

(a) 3
(b) 8
(c) 11
(d) 14

155. The dissociation constant of *HCN* is 5×10^{-10}. The pH of the solution prepared by mixing 1.5 *mole* of *HCN* and 0.15 *moles* of *KCN* in water and making up the total volume to $0.5 dm^3$ is **[JIPMER 2001]**

(a) 7.302 (b) 9.302
(c) 8.302 (d) 10.302

156. Which buffer solution out of the following will have $pH > 7$ **[MP PET 2001]**

(a) $CH_3COOH + CH_3COONa$
(b) $HCOOH + HCOOK$
(c) CH_3COONH_4
(d) $NH_4OH + NH_4Cl$

157. The pK_a of equimolecular sodium acetate and acetic acid mixture is 4.74. If pH is **[DPMT 2001]**

(a) 7 (b) 9.2
(c) 4.74 (d) 14

158. pH of $NaCl$ solution is **[CET Pune 1998]**

(a) 7 (b) Zero
(c) >7 (d) <7

159. A solution of sodium chloride in contact with atmosphere has a pH of about **[NCERT 1972, 77]**

(a) 3.5 (b) 5
(c) 7 (d) 1.4

160. Which would decrease the pH of $25 cm^3$ of a $0.01 M$ solution of hydrochloric acid **[MH CET 2001]**

(a) The addition of $25 cm^3$ $0.005 M$ hydrochloric acid
(b) The addition of $25 cm^3$ of $0.02 M$ hydrochloric acid
(c) The addition of magnesium metal
(d) None of these

161. The condition for minimum change in pH for a buffer solution is **[RPMT 2000]**

(a) Isoelectronic species are added
(b) Conjugate acid or base is added
(c) $pH = pK_a$
(d) None of these

162. A buffer solution with pH 9 is to be prepared by mixing NH_4Cl and NH_4OH. Calculate the number of moles of NH_4Cl that should be added to one litre of $1.0 M\ NH_4OH$. $[K_b = 1.8 \times 10^{-5}]$ **[UPSEAT 2001]**

(a) 3.4 (b) 2.6
(c) 1.5 (d) 1.8

163. The ionization constant of a certain weak acid is 10^{-4}. What should be the [salt] to [acid] ratio if we have to prepare a buffer with *pH* = 5 using this acid and one of the salts **[CPMT 2000; KCET 2000; Pb. CET 2000]**

(a) $1:10$ (b) $10:1$
(c) $5:4$ (d) $4:5$

164. Which solution has the highest *pH* value **[JIPMER 2000]**

(a) $1M\ KOH$
(b) $1M\ H_2SO_4$
(c) Chlorine water
(d) Water containing carbon dioxide

165. One weak acid (like CH_3COOH) and its strong base together with salt (like CH_3COONa) is a buffer solution. In which pair this type of characteristic is found **[AIIMS 1982; CPMT 1994; MP PET 1994]**

(a) HCl and $NaCl$ (b) $NaOH$ and $NaNO_3$
(c) KOH and KCl (d) NH_4OH and NH_4Cl

166. If the *pH* of a solution of an alkali metal hydroxide is 13.6, the concentration of hydroxide is **[JIPMER 2000]**

(a) Between 0.1 *M* and 1 *M*
(b) More than 1 *M*
(c) Less than 0.001 *M*
(d) Between 0.01 *M* and 1 *M*

167. The pK_a of acetylsalicylic acid (aspirin) is 3.5. The pH of gastric juice in human stomach is about 2-3 and the pH in the small intestine is about 8. Aspirin will be **[IIT 1988; KCET 2003]**

(a) Unionized in the small intestine and in the stomach
(b) Completely ionized in the small intestine and in the stomach
(c) Ionized in the stomach and almost unionized in the small intestine
(d) Ionized in the small intestine and almost unionized in the stomach

168. The concentration of hydrogen ion in water is **[MP PET 1990]**

(a) 8 (b) 1×10^{-7}
(c) 7 (d) $1/7$

169. pH of a 10 M solution of HCl is **[CBSE PMT 1995]**

(a) Less than 0 (b) 2
(c) 0 (d) 1

170. The pH of $1\ N\ H_2O$ is **[CPMT 1988]**

(a) 7 (b) >7
(c) <7 (d) 0

171. If H^+ ion concentration of a solution is increased by 10 times its *pH* will be **[DCE 2000]**

(a) Increase by one (b) Remains unchanged
(c) Decrease by one (d) Increase by 10

172. The gastric juice in our stomach contains enough HCl to make the hydrogen ion concentration about $0.01\, mole/litre$ The pH of gastric juice is **[NCERT 1974]**
(a) 0.01 (b) 1
(c) 2 (d) 14

173. Addition of which chemical will decrease the hydrogen ion concentration of an acetic acid solution **[MP PMT 1990]**
(a) NH_4Cl (b) $Al_2(SO_4)_3$
(c) $AgNO_3$ (d) HCN

174. The one which has the highest value of pH is
(a) Distilled water
(b) NH_3 solution in water
(c) NH_3
(d) Water saturated with Cl_2

175. The solution of Na_2CO_3 has pH **[AMU 1988]**
(a) Greater than 7 (b) Less than 7
(c) Equal to 7 (d) Equal to zero

176. Which is not a buffer solution **[CPMT 1990]**
(a) $NH_4Cl + NH_4OH$
(b) $CH_3COOH + CH_3COONa$
(c) CH_3COONH_4
(d) Borax + Boric acid

177. What will be hydrogen ion concentration in moles $litre^{-1}$ of a solution, whose pH is 4.58 **[UPSEAT 2001]**
(a) 2.63×10^{-5} (b) 3.0×10^{-5}
(c) 4.68 (d) None of these

178. Assuming complete dissociation, the pH of a 0.01 M $NaOH$ solution is equal to
[NCERT 1975; CPMT 1977; DPMT 1982; BHU 1997]
(a) 2.0 (b) 14.0
(c) 12.0 (d) 0.01

179. 50 ml of $2N$ acetic acid mixed with $10ml$ of $1N$ sodium acetate solution will have an approximate pH of
[MP PMT/PET 1988]
(a) 4 (b) 5
(c) 6 (d) 7

180. The hydrogen ion concentration of 0.001 M $NaOH$ solution is **[AFMC 1983]**
(a) $1 \times 10^{-2} mole/litre$ (b) $1 \times 10^{-11} mole/litre$
(c) $1 \times 10^{-14} mole/litre$ (d) $1 \times 10^{-12} mole/litre$

181. A weak monoprotic acid of 0.1 *M*, ionizes to 1% in solution. What will be the pH of solution **[MNR 1988]**
(a) 1 (b) 2
(c) 3 (d) 11

182. pH of a solution is 4. The hydroxide ion concentration of the solution would be
[NCERT 1981; CBSE PMT 1991; MP PMT 1994]
(a) 10^{-4} (b) 10^{-10}
(c) 10^{-2} (d) 10^{-12}

183. The pH of an aqueous solution containing $[H^+] = 3 \times 10^{-3} M$ is **[MP PET 2001,04]**
(a) 2.471 (b) 2.523
(c) 3.0 (d) – 3

184. pH of blood is maintained constant by mechanism of
[MH CET 2002]
(a) Common ion effect (b) Buffer
(c) Solubility (d) All of these

185. The *pH* of normal *KOH* is **[MP PET 1990]**
(a) 1 (b) 0
(c) 14 (d) 7

186. The concentration of hydrogen ion $[H^+]$ in 0.01 *M* HCl is
[EAMCET 1979]
(a) 10^{12} (b) 10^{-2}
(c) 10^{-1} (d) 10^{-12}

187. A solution of weak acids is diluted by adding an equal volume of water. Which of the following will not change
[JIPMER 1997]
(a) Strength of the acid
(b) The value of $[H_3O^+]$
(c) pH of the solution
(d) The degree of dissociation of acid

188. Ka of H_2O_2 is of the order of **[DCE 2004]**
(a) 10^{-12} (b) 10^{-14}
(c) 10^{-16} (d) 10^{-10}

189. Equivalent weight of an acid **[UPSEAT 2004]**
(a) Depends on the reaction involved
(b) Depends upon the number of oxygen atoms present
(c) Is always same
(d) None of the above

190. pH scale was introduced by **[UPSEAT 2004]**
(a) Arrhenius (b) Sorensen
(c) Lewis (d) Lowry

191. Buffer solution is prepared by mixing **[MH CET 2003]**
(a) Strong acid + its salt of strong base
(b) Weak acid + its salt of weak base
(c) Strong acid + its salt of weak base
(d) Weak acid + its salt of strong base

192. The *pH* of millimolar *HCl* is **[MH CET 2004]**
(a) 1 (b) 3
(c) 2 (d) 4

193. Which of the following is a Lewis base **[CPMT 2004]**

(a) NaOH (b) NH_3
(c) BCl_3 (d) All of these

194. What will be the pH value of 0.05 M $Ba(OH)_2$ solution **[CPMT 2004]**
(a) 12 (b) 13
(c) 1 (d) 12.96

195. In a mixing of acetic acid and sodium acetate the ratio of concentration of the salts to the acid is increased ten times. Then the pH of the solution **[KCET 2004]**
(a) Increase by one (b) Decreases by one
(c) Decrease ten fold (d) Increases ten fold

196. The rapid change of pH near the stoichiometric point of an acid-base titration is the basis of indicator detection. pH of the solution is related to ratio of the concentrations of the conjugate acid (HIn) and base (In^-) forms of the indicator by the expression **[CBSE PMT 2004]**
(a) $\log\frac{[HIn]}{[In^-]} = pH - pK_{In}$ (b) $\log\frac{[In^-]}{[HIn]} = pH - pK_{In}$
(c) $\log\frac{[In^-]}{[HIn]} = pK_{In} - pH$ (d) $\log\frac{[HIn]}{[In^-]} = pK_{In} - pH$

197. Which of the following statement(s) is(are) correct **[IIT 1998]**
(a) The pH of 1.0×10^{-8} M solution of HCl is 8
(b) The conjugate base of $H_2PO_4^-$ is HPO_4^{2-}
(c) Autoprotolysis constant of water increases with temperature
(d) When a solution of a weak monoprotic acid is titrated against a strong base, at half neutralization point $pH = \frac{1}{2} pK_a$

198. An aqueous solution of sodium carbnate has a pH greater than 7 becaue **[DCE 2003]**
(a) It contains more carbonate ions than H_2O molecules
(b) Contains more hydroxide ions than carbonate ions
(c) Na^+ ions react with water
(d) Carbonate ions react with H_2O

199. A pH of 7 signifies **[CPMT 1974; DPMT 1982]**
(a) Pure water (b) Neutral solution
(c) Basic solution (d) Acidic solution

200. Assuming complete dissociation, which of the following aqueous solutions will have the same pH value **[Roorkee Qualifying 1998]**
(a) $100 ml$ of $0.01\ M\ HCl$
(b) $100 ml$ of $0.01\ M\ H_2SO_4$
(c) $50\ ml$ of $0.01\ M\ HCl$
(d) Mixture of 50 ml of $0.02\ M\ H_2SO_4$ and $50\ ml$ of $0.02\ M\ NaOH$

201. A buffer solution can be prepared from a mixture of **[IIT 1999; KCET 1999; MP PMT 2002]**
(a) Sodium acetate and acetic acid in water
(b) Sodium acetate and hydrochloric acid in water
(c) Ammonia and ammonium chloride in water
(d) Ammonia and sodium hydroxide in water

202. Which of the following will not function as a buffer solution **[Roorkee 2000]**
(a) $NaCl$ and $NaOH$
(b) $NaOH$ and NH_4OH
(c) CH_3COONH_4 and HCl
(d) Borax and boric acid

203. Which one of the following statements is not true **[AIEEE 2003]**
(a) The conjugate base of $H_2PO_4^-$ is HPO_4^{2-}
(b) $pH + pOH = 14$ for all aqueous solutions
(c) The pH of $1 \times 10^{-8} M\ HCl$ is 8
(d) 96,500 coulombs of electricity when passed through a $CuSO_4$ solution deposits 1 *gram* equivalent of copper at the cathode

204. The pH value of $0.1\ M\ HCl$ is approximately 1. What will be the approximate pH value of 0.05 $M\ H_2SO_4$ **[MP PMT 1991]**
(a) 0.05 (b) 0.5
(c) 1 (d) 2

205. The K_{sp} of $Mg(OH)_2$ is $1 \times 10^{-12}, 0.01 M\ Mg(OH)_2$ will precipitate at the limiting pH **[DPMT 2005]**
(a) 3 (b) 9
(c) 5 (d) 8

206. The pH of an aqueous solution having hydroxide ion concentration as 1×10^{-5} is **[MP PMT 1991]**
(a) 5 (b) 9
(c) 4.5 (d) 11

CT Critical Thinking

Objective Questions

1. The K_{SP} of AgI is 1.5×10^{-16}. On mixing equal volumes of the following solutions, precipitation will occur only with **[AMU 2000]**

(a) $10^{-7} M\ Ag^+$ and $10^{-19} M\ I^-$

(b) $10^{-8} M\ Ag^+$ and $10^{-8} M\ I^-$

(c) $10^{-16} M\ Ag^+$ and $10^{-16} M\ I^-$

(d) $10^{-9} M\ Ag^+$ and $10^{-9} M\ I^-$

2. The strongest Bronsted base in the following anion is **[IIT 1981; MP PET 1992, 97; MP PMT 1994; RPMT 1999; KCET 2000; AIIMS 2001; UPSEAT 2002; AFMC 2002; Pb. CET 2004]**

(a) ClO^- (b) ClO_2^-

(c) ClO_3^- (d) ClO_4^-

3. Which one of the following compound is not a protonic acid **[CBSE PMT 2003]**

(a) $SO_2(OH)_2$ (b) $B(OH)_3$

(c) $PO(OH)_3$ (d) $SO(OH)_2$

4. Calculate the hydrolysis constant of the salt containing NO_2. Given the K_a for HNO_2 $= 4.5\times10^{-10}$ **[UPSEAT 2001]**

(a) 2.22×10^{-5} (b) 2.02×10^{5}

(c) 4.33×10^{4} (d) 3.03×10^{-5}

5. The molar solubility $(mol L^{-1})$ of a sparingly soluble salt MX_4 is $'S'$. The corresponding solubility product is K_{sp}. $'S'$ is given in terms of K_{sp} by the relation **[AIEEE 2004]**

(a) $s = (256K_{sp})^{1/5}$ (b) $s = (128K_{sp})^{1/4}$

(c) $s = (K_{sp}/128)^{1/4}$ (d) $s = (K_{sp}/256)^{1/5}$

6. Electrophiles are **[RPET 2000]**

(a) Lewis acids (b) Lewis base

(c) Bronsted acid (d) Bronsted base

7. Total number of moles for the reaction $2HI \rightleftarrows H_2 + I_2$. if α is degree of dissociation is **[CBSE PMT 1996]**

(a) 2 (b) $2-\alpha$

(c) 1 (d) $1-\alpha$

8. Which one is a Lewis acid **[RPMT 1997]**

(a) ClF_3 (b) H_2O

(c) NH_3 (d) None of these

9. Heat of neutralisation of weak acid and strong base is less than the heat of neutralisation of strong acid and strong base due to **[KCET 2002]**

(a) Energy has to be spent for the total dissociation of weak acid

(b) Salt of weak acid and strong base is not stable

(c) Incomplete dissociation of weak acid

(d) Incomplete neutralisation of weak acid

10. pK_a values of two acids *A* and *B* are 4 and 5. The strengths of these two acids are related as **[KCET 2001]**

(a) Acid *A* is 10 times stronger than acids *B*

(b) Strength of acid *A* : strengtha of acid $B = 4:5$

(c) The strengths of the two acids can not be compared

(d) Acid *B* is 10 times stronger than acid *A*

11. The dissociation constant of two acids HA_1 and HA_2 are 3.14×10^{-4} and 1.96×10^{-5} respectively. The relative strength of the acids will be approximately **[RPMT 2000]**

(a) 1 : 4 (b) 4 : 1

(c) 1 : 16 (d) 16 : 1

12. An aqueous solution of ammonium acetate is **[NCERT 1980, 81; RPMT 1999]**

(a) Faintly acidic (b) Faintly basic

(c) Fairly acidic (d) Almost neutral

13. The dissociation constant of a weak acid is 1.0×10^{-5}, the equilibrium constant for the reaction with strong base is **[MP PMT 1990]**

(a) 1.0×10^{-5} (b) 1.0×10^{-9}

(c) 1.0×10^{9} (d) 1.0×10^{14}

14. The pH of $0.1\ M$ solution of the following salts increases in the order **[IIT 1999]**

(a) $NaCl < NH_4Cl < NaCN < HCl$

(b) $HCl < NH_4Cl < NaCl < NaCN$

(c) $NaCN < NH_4Cl < NaCl < HCl$

(d) $HCl < NaCl < NaCN < NH_4Cl$

15. Which of the following is the strongest acid **[AMU 1999; MH CET 1999, 2002]**

(a) $SO(OH)_2$ (b) $SO_2(OH)_2$

(c) $ClO_3(OH)$ (d) $PO(OH)_3$

16. The strongest of the four acids listed below is **[NCERT 1984]**

(a) $HCOOH$ (b) CH_3COOH

(c) $ClCH_2COOH$ (d) FCH_2COOH

17. Which equilibrium can be described as an acid-base reaction using the Lewis acid-base definition but not using the Bronsted-Lowry definition **[AIIMS 1980]**

(a) $2NH_3 + H_2SO_4 \rightleftarrows 2NH_4^+ + SO_4^{2-}$

(b) $NH_3 + CH_3COOH \rightleftarrows NH_4^+ + CH_3COO^-$

(c) $H_2O + CH_3COOH \rightleftarrows H_3O^+ + CH_3COO^-$

(d) $[Cu(H_2O)_4]^{2+} + 4NH_3 \rightleftarrows$
$[Cu(NH_3)_4]^{2+} + 4H_2O$

18. The hydride ion H^- is stronger base than its hydroxide ion OH^-. Which of the following reaction will occur if sodium hydride (NaH) is dissolved in water **[CBSE PMT 1997]**

(a) $H^-(aq) + H_2O \rightarrow H_2O$

(b) $H^-(aq) + H_2O(l) \rightarrow OH^- + H_2$

(c) $H^- + H_2O \rightarrow$ No reaction

(d) None of these

19. Dissociation constant of a weak acid is 1×10^{-4}. Equilibrium constant of its reaction with strong base is **[UPSEAT 2003]**

(a) 1×10^{-4} (b) 1×10^{10}

(c) 1×10^{-10} (d) 1×10^{14}

20. Arrange the acids (I) H_2SO_3 (II) H_3PO_3 and (III) $HClO_3$ in the decreasing order of acidity **[UPSEAT 2001]**

(a) I > III > II (b) I > II > III

(c) II > III > I (d) III > I > II

21. Self-ionisation of liquid ammonia occurs as, $2NH_3 \rightleftarrows NH_4^+ + NH_2^-; K = 10^{-10}$. In this solvent, an acid might be **[JIPMER 2001]**

(a) NH_4^+

(b) NH_3

(c) Any species that will form NH_4^+

(d) All of these

22. $\Delta H_f(H_2O) = X;$ Heat of neutralisation of CH_3COOH and $NaOH$ will be **[BHU 2003]**

(a) Less than 2*X* (b) Less than *X*

(c) *X* (d) Between *X* and 2*X*

23. Which of the following oxides will not give OH^- in aqueous solution **[NCERT 1980]**

(a) Fe_2O_3 (b) MgO

(c) Li_2O (d) K_2O

24. A precipitate of CaF_2 $(K_{sp} = 1.7 \times 10^{-10})$ will be obtained when equal volume of the following are mixed

[MP PMT 1990, 95; IIT 1982; MNR 1992]

(a) $10^{-4} M\, Ca^{2+}$ and $10^{-4} M\, F^-$

(b) $10^{-2} M\, Ca^{2+}$ and $10^{-3} M\, F^-$

(c) $10^{-5} M\, Ca^{2+}$ and $10^{-3} M\, F^-$

(d) $10^{-3} M\, Ca^{2+}$ and $10^{-5} M\, F^-$

25. The degree of hydrolysis of a salt of weak acid and weak base in its 0.1 *M* solution is found to be 50%. If the molarity of the solution is 0.2 *M*, the percentage hydrolysis of the salt should be **[AMU 1999]**

(a) 50% (b) 35%

(c) 75% (d) 100%

26. The pH of 0.1 *M* solution of a weak monoprotic acid 1% ionized is **[UPSEAT 2001; Pb. PMT 2001]**

(a) 1 (b) 2

(c) 3 (d) 4

27. Which one is the strongest acid

[MH CET 1999; AMU 1999,2000; Pb.CET 2001,03; MP PET 2001]

(a) $HClO$ (b) $HClO_2$

(c) H_2SO_4 (d) $HClO_4$

28. Which of the following is Lewis acid **[Pb. CET 2000]**

(a) S (b) $:CH_2$

(c) $(CH_3)_3B$ (d) All of these

29. The solubility product of $Mg(OH)_2$ is 1.2×10^{-11}. The solubility of this compound in gram per $100 cm^3$ of solution is

[Roorkee 2000]

(a) 1.4×10^{-4} (b) 8.16×10^{-4}

(c) 0.816 (d) 1.4

30. What is $[H^+]$ of a solution that is $0.01M$ in HCN and $0.02M$ in $NaCN$

$(K_a$ for $HCN = 6.2 \times 10^{-10})$

[MP PMT 2000]

(a) 3.1×10^{10} (b) 6.2×10^{5}

(c) 6.2×10^{-10} (d) 3.1×10^{-10}

31. Which is neucleophile **[DPMT 2001; RPMT 2002]**

(a) BF_3 (b) NH_3

(c) $BeCl_2$ (d) H_2O

32. The solubility of $CuBr$ is $2 \times 10^{-4} mol/l$ at $25^\circ C$. The K_{sp} value for $CuBr$ is

[AIIMS 2002]

(a) $4 \times 10^{-8} mol^2 l^{-2}$ (b) $4 \times 10^{-11} mol^2 L^{-1}$

(c) $4 \times 10^{-4} mol^2 l^{-2}$ (d) $4 \times 10^{-15} mol^2 l^{-2}$

33. A 0.004 *M* solution of Na_2SO_4 is isotonic with a 0.010 *M* solution of glucose at same temperature. The apparent degree of disociation of Na_2SO_4 is

[IIT JEE Screening 2004]

(a) 25% (b) 50%

(c) 75% (d) 85%

34. K_{sp} for $Cr(OH)_3$ is 2.7×10^{-31}. What is its solubility in *moles / litre*. **[JEE Orissa 2004]**

(a) 1×10^{-8} (b) 8×10^{-8}

(c) 1.1×10^{-8} (d) 0.18×10^{-8}

35. pK_a of acetic acid is 4.74. The concentration of CH_3COONa is 0.01 *M*. The *p*H of CH_3OONa is **[Orissa JEE 2004]**

(a) 3.37 (b) 4.37

(c) 4.74 (d) 0.474

36. If the solubility product of $AgBrO_3$ and Ag_2SO_4 are 5.5×10^{-5} and 2×10^{-5} respectively, the relationship between the solubilities of these can be correctly represented as **[EAMCET 1985]**

(a) $S_{AgBrO_3} > S_{Ag_2SO_4}$ (b) $S_{AgBrO_3} < S_{Ag_2SO_4}$

(c) $S_{AgBrO_3} = S_{Ag_2SO_4}$ (d) $S_{AgBrO_3} \approx S_{Ag_2SO_4}$

37. The ionisation constant of phenol is higher than that of ethanol because **[JIPMER 2002]**

(a) Phenoxide ion is bulkier than ethanoxide

(b) Phenoxide ion is stronger base than ethanoxide

(c) Phenoxide ion is stabilised through delocalisation

(d) Phenoxide ion is less stable than ethoxide

38. A weak acid *HX* has the dissociation constant $1 \times 10^{-5} M$. It forms a salt *NaX* on reaction with alkali. The degree of hydrolysis of 0.1 *M* solution of *NaX* is

[IIT JEE Screening 2004]

(a) 0.0001% (b) 0.01%

(c) 0.1% (d) 0.15%

39. In the equilibrium $A^- + H_2O \rightleftharpoons HA + OH^-$ $(K_a = 1.0 \times 10^{-5})$. The degree of hydrolysis of 0.001 *M* solution of the salt is **[AMU 1999]**

(a) 10^{-3} (b) 10^{-4}

(c) 10^{-5} (d) 10^{-6}

40. The sulphide ion concentration $[S^{2-}]$ in saturated H_2S solution is 1×10^{-22}. Which of the following sulphides should be quantitatively precipitated by H_2S in the presence of dil. HCl

Sulphide	**Solubility Product**
(I)	1.4×10^{-16}
(II)	1.2×10^{-22}
(III)	8.2×10^{-46}
(IV)	5.0×10^{-34}

(a) I, II (b) III, IV

(c) II, III, IV (d) Only I

41. When equal volumes of the following solutions are mixed, precipitation of $AgCl (K_{sp} = 1.8 \times 10^{-10})$ will occur only with

[IIT 1988; CBSE PMT PMT 1992; DCE 2000]

(a) $10^{-4} M\ Ag^+$ and $10^{-4} M\ Cl^-$

(b) $10^{-5} M\ Ag^+$ and $10^{-5} M\ Cl^-$

(c) $10^{-6} M\ Ag^+$ and $10^{-6} M\ Cl^-$

(d) $10^{-10} M\ Ag^+$ and $10^{-10} M\ Cl^-$

42. K_{sp} of an electrolyte *AB* is 1×10^{-10}. $[A^+] = 10^{-5} M$, which concentration of B^- will not give precipitate of *AB*

[BHU 2003]

(a) 5×10^{-6} (b) 1×10^{-5}

(c) 2×10^{-5} (d) 5×10^{-5}

43. One litre of water contains $10^{-7} mole$ hydrogen ions. The degree of ionization in water will be **[CPMT 1985, 88, 93]**

(a) $1.8 \times 10^{-7}\%$ (b) $0.8 \times 10^{-9}\%$

(c) $3.6 \times 10^{-7}\%$ (d) $3.6 \times 10^{-9}\%$

44. If the solubility products of $AgCl$ and $AgBr$ are 1.2×10^{-10} and 3.5×10^{-13} respectively, then the relation between the solubilities (denoted by the symbol 'S') of these

salts can correctly be represented as **[MP PET 1994]**

(a) S of $AgBr$ is less than that of $AgCl$

(b) S of $AgBr$ is greater than that of $AgCl$

(c) S of $AgBr$ is equal to that of $AgCl$

(d) S of $AgBr$ is 10^6 times greater than that of $AgCl$

45. If the solubility product of lead iodide (PbI_2) is 3.2×10^{-8}, then its solubility in moles/litre will be **[MP PMT 1990]**

(a) 2×10^{-3} (b) 4×10^{-4}

(c) 1.6×10^{-5} (d) 1.8×10^{-5}

46. Calculate the solubility of $AgCl$(s) in $0.1 M\ NaCl$ at $25^\circ C$. $K_{sp}(AgCl) = 2.8 \times 10^{-10}$

[UPSEAT 2001]

(a) $3.0 \times 10^{-8} ML^{-1}$ (b) $2.5 \times 10^{-7} ML^{-1}$

(c) $2.8 \times 10^{-9} ML^{-1}$ (d) $2.5 \times 10^{7} ML^{-1}$

47. The solubility product of a binary weak electrolyte is 4×10^{-10} at $298K$. Its solubility in mol dm^{-3} at the same temperature is **[KCET 2001]**

(a) 4×10^{-5} (b) 2×10^{-5}

(c) 8×10^{-10} (d) 16×10^{-20}

48. Solubility of $AgCl$ at 20^0C is 1.435×10^{-3} gm per litre. The solubility product of $AgCl$ is **[CPMT 1989; BHU 1997; AFMC 2000; CBSE PMT 2002]**

(a) 1×10^{-5} (b) 1×10^{-10}

(c) 1.435×10^{-5} (d) 108×10^{-3}

49. pK_a value for acetic acid at the experimental temperature is 5. The percentage hydrolysis of $0.1\ M$ sodium acetate solution will be

(a) 1×10^{-4} (b) 1×10^{-2}

(c) 1×10^{-3} (d) 1×10^{-5}

50. At 30^oC, the solubility of $Ag_2CO_3 (K_{sp}=8\times10^{-12})$ would be greatest in one litre of **[MP PMT 1990]**

(a) $0.05M\ Na_2CO_3$ (b) $0.05M\ AgNO_3$

(c) Pure water (d) $0.05M\ NH_3$

51. The values of K_{sp} for CuS, Ag_2S and HgS are $10^{-31}, 10^{-42}$ and 10^{-54} respectively. The correct order of their solubility in water is **[MP PMT 2003]**

(a) $Ag_2S > HgS > CuS$ (b) $HgS > CuS > Ag_2S$

(c) $HgS > Ag_2S > CuS$ (d) $Ag_2S > CuS > HgS$

52. The *pH* of a soft drink is 3.82. Its hydrogen ion concentration will be **[MP PET 1990]**

(a) $1.96\times10^{-2}\ mol/l$ (b) $1.96\times10^{-3}\ mol/l$

(c) $1.5\times10^{-4}\ mol/l$ (d) $1.96\times10^{-1}\ mol/l$

53. The *pH* of a solution at $25^\circ C$ containing $0.10m$ sodium acetate and $0.03m$ acetic acid is (pK_a for $CH_3COOH=4.57$) **[AIIMS 2002; BHU 2002]**

(a) 4.09 (b) 5.09

(c) 6.10 (d) 7.09

54. A weak acid is 0.1% ionised in 0.1 *M* solution. Its *pH* is **[BVP 2004]**

(a) 2 (b) 3

(c) 4 (d) 1

55. The solubility product of As_2S_3 is 2.8×10^{-72}. What is the solubility of As_2S_3 **[Pb. CET 2003]**

(a) 1.09×10^{-15} mole/litre

(b) 1.72×10^{-15} mole/litre

(c) 2.3×10^{-16} mole/litre

(d) 1.65×10^{-36} mole/litre

56. For a weak acid HA with dissociation constant 10^{-9}, pOH of its 0.1 *M* solution is **[CBSE PMT 1989]**

(a) 9 (b) 3

(c) 11 (d) 10

57. The dissociation of water at 25^0C is $1.9\times10^{-7}\%$ and the density of water is $1.0\,g/cm^3$. The ionisation constant of water is **[IIT 1995]**

(a) 3.42×10^{-6} (b) 3.42×10^{-8}

(c) 1.00×10^{-14} (d) 2.00×10^{-16}

58. What is the *p*H of 0.01 *M* glycine solution? For glycine, $Ka_1=4.5\times10^{-3}$ and $Ka_2=1.7\times10^{-10}$ at 298 *K* **[AIIMS 2004]**

(a) 3.0 (b) 10.0

(c) 6.1 (d) 7.2

59. The concentration of $[H^+]$ and concentration of $[OH^-]$ of a 0.1 aqueous solution of 2% ionised weak acid is

[Ionic product of water $=1\times10^{-14}$] **[DPMT 2004; CBSE PMT 1999]**

(a) $2\times10^{-3}M$ and $5\times10^{-12}M$

(b) $1\times10^{3}\ M$ and $3\times10^{-11}M$

(c) $0.02\times10^{-3}\ M$ and $5\times10^{-11}M$

(d) $3\times10^{-2}\ M$ and $4\times10^{-13}M$

60. If solubility product of $HgSO_4$ is 6.4×10^{-5}, then its solubility is **[BHU 2004]**

(a) 8×10^{-3} mole/litre (b) 6.4×10^{-5} mole/litre

(c) 6.4×10^{-3} mole/litre (d) 2.8×10^{-6} mole/litre

61. At 298*K* a 0.1 *M* CH_3COOH solution is 1.34% ionized. The ionization constant K_a for acetic acid will be **[AMU 2002; AFMC 2005]**

(a) 1.82×10^{-5} (b) 18.2×10^{-5}

(c) 0.182×10^{-5} (d) None of these

62. Hydrogen ion concentration of an aqueous solution is $1\times10^{-4}M$. The solution is diluted with equal volume of water. Hydroxyl ion concentration of the resultant solution in terms of *mol* dm^{-3} is **[KCET 2001]**

(a) 1×10^{-8} (b) 1×10^{-6}

(c) 2×10^{-10} (d) 0.5×10^{-10}

63. Which one of the following is not a buffer solution **[AIIMS 2003]**

(a) $0.8M\ H_2S + 0.8M\ KHS$

(b) $2M\ C_6H_5NH_2 + 2M\ C_6H_5\overset{+}{N}H_3Br$

(c) $3M\ H_2CO_3 + 3M\ KHCO_3$

(d) $0.05M\ KClO_4 + 0.05M\ HClO_4$

64. The hydrogen ion concentration of a $0.006M$ benzoic acid solution is $(K_a=6\times10^{-5})$ **[MP PET 1994]**

(a) 0.6×10^{-4}
(b) 6×10^{-4}
(c) 6×10^{-5}
(d) 3.6×10^{-4}

65. Calculate the amount of $(NH_4)_2SO_4$ in grams which must be added to 500 *ml* of $0.200M\ NH_3$ to yield a solution with $pH=9.35$ $(K_b$ for $NH_3=1.78\times10^{-5})$ **[UPSEAT 2001]**

(a) 10.56 *gm*
(b) 15 *gm*
(c) 12.74 *gm*
(d) 16.25 *gm*

66. *pH* of a solution produced when an aqueous solution of pH 6 is mixed with an equal volume of an aqueous solution of pH 3 is about **[KCET 2001]**

(a) 3.3
(b) 4.3
(c) 4.0
(d) 4.5

67. Calculate the H^+ ion concentration in a $1.00\,(M)$ HCN *litre* solution $(K_a=4\times10^{-10})$

[Bihar CEE 1995]

(a) 4×10^{-14} *mole/litre*
(b) 2×10^{-5} *mole/litre*
(c) 2.5×10^{-5} *mole/litre*
(d) None of these

68. The number of moles of hydroxide (OH^-) ion in 0.3 *litre* of 0.005 *M* solution of $Ba(OH)_2$ is

[JIPMER 2001]

(a) 0.0050
(b) 0.0030
(c) 0.0015
(d) 0.0075

69. The *pH* of pure water or neutral solution at $50^\circ C$ is .... $(pK_w=13.26=13.26$ at $50^\circ C)$

[Pb. PMT 2002; DPMT 2002]

(a) 7.0
(b) 7.13
(c) 6.0
(d) 6.63

70. *pH* of 0.1 *M* solution of a weak acid (*HA*) is 4.50. It is neutralised with $NaOH$ solution to decrease the acid content to half *pH* of the resulting solution

[JIPMER 2002]

(a) 4.50
(b) 8.00
(c) 7.00
(d) 10.00

71. If $50ml$ of $0.2M\ KOH$ is added to $40ml$ of $0.5M\ HCOOH$, the pH of the resulting solution is $(K_a=1.8\times10^{-4})$

[MH CET 2000]

(a) 3.4
(b) 7.5
(c) 5.6
(d) 3.75

72. The Bronsted acids in the reversible reaction are

$$HCO_3^-(aq)+OH^-(aq)\rightleftarrows CO_3^{2-}(aq)+H_2O$$

[DPMT 2002]

(a) OH^- and CO_3^{2-}
(b) OH^- and H_2O
(c) HCO_3^- and H_2O
(d) HCO_3^- and CO_3^{2-}

73. A 0.1*N* solution of an acid at room temperature has a degree of ionisation 0.1. The concentration of OH^- would be **[MH CET 1999]**

(a) $10^{-12}M$
(b) $10^{-11}M$
(c) $10^{-9}M$
(d) $10^{-2}M$

74. Increasing order of acidic character would be **[RPMT 1999]**

(a) $CH_3COOH<H_2SO_4<H_2CO_3$
(b) $CH_3COOH<H_2CO_3<H_2SO_4$
(c) $H_2CO_3<CH_3COOH<H_2SO_4$
(d) $H_2SO_4<H_2CO_3<CH_3COOH$

75. The correct order of increasing $[H_3O^+]$ in the following aqueous solutions is **[UPSEAT 2000]**

(a) 0.01 *M* H_2S <0.01 *M* H_2SO_4 < 0.01 *M* $NaCl$ < 0.01 $M\ NaNO_2$
(b) 0.01 *M* $NaCl$ <0.01 *M* $NaNO_2$ < 0.01 *M* H_2S < 0.01 *M* H_2SO_4
(c) 0.01 *M* $NaNO_2$ <0.01 *M* $NaCl$ < 0.01 *M* H_2S < 0.01 *M* H_2SO_4
(d) 0.01 *M* H_2S < 0.01 *M* $NaNO_2$ < 0.01 *M* $NaCl$ < 0.01 *M* H_2SO_4

76. A base dissolved, in water, yields a solution with a hydroxyl ion concentration of $0.05\,mol\,litre^{-1}$. The solution is

[CBSE PMT 2000]

(a) Basic
(b) Acid
(c) Neutral
(d) Either (b) or (c)

77. In the given reaction, the oxide of sodium is ....

$$\begin{bmatrix} 4Na+O_2\rightarrow 2Na_2O \\ Na_2O+H_2O\rightarrow 2NaOH \end{bmatrix}$$

[Orissa JEE 2002]

(a) Acidic
(b) Basic
(c) Amphoteric
(d) Neutral

78. What is the *pH* of a 1*M* CH_3COOH a solution K_a of acetic acid $=1.8\times10^{-5}$.

$K=10^{-14}mol^2litre^{-2}$ **[DPMT 2002]**

(a) 9.4
(b) 4.8
(c) 3.6
(d) 2.4

AR Assertion & Reason

For AIIMS Aspirants

Read the assertion and reason carefully to mark the correct option out of the options given below :

(a) If both assertion and reason are true and the reason is the correct explanation of the assertion.
(b) If both assertion and reason are true but reason is not the correct explanation of the assertion.
(c) If assertion is true but reason is false.
(d) If the assertion and reason both are false.
(e) If assertion is false but reason is true.

1. Assertion : *p*H of hydrochloric acid solution is less than that of acetic acid solution of the same concentration.
Reason : In equimolar solutions, the number of titrable protons present in hydrochloric acid is less than that persent in acetic acid.
[NDA 1999]

2. Assertion : A ionic product is used fro any types of electrolytes whereas solubility product is applicable only to sparingly soluble salts.
Reason : Ionic product is defined at any stage of the raction whereas solubility product is only appicable to the saturation stage.
[AIIMS 2001]

3. Assertion : A solution of $FeCl_3$ in water produce brown precipitate on standing.
Reason : Hydrolysis of $FeCl_3$ takes place in water

4. Assertion : $BaCO_3$ is more soluble in HNO_3 than in plain water.
Reason : Carbonate is a weak base and reacts with the H^+ from the strong acid, casuing the barium salt to dissociate.

5. Assertion : $CHCl_3$ is more acidic than CHF_3.
Reason : The conjugate base of $CHCl_3$ is more stable than CHF_3.

6. Assertion : Addition of silver ions to a mixture of aqueous sodium chloride and sodium bromide solution will first precipitate $AgBr$ rather than $AgCl$.
Reason : K_{sp} of $AgCl < K_{sp}$ of $AgBr$. **[AIIMS 2004]**

7. Assertion : The pK_a of acetic acid is lower than that of phenol.
Reason : Phenoxide ion is more resonance stabilized. **[AIIMS 2004]**

8. Assertion : *Sb* (III) is not precipitated as sulphide when in its alkaline solution H_2S is passed.
Reason : The concentration of S^{2-} ion in alkaline medium is inadequate for precipitation.
[AIIMS 2004]

9. Assertion : Ionic reactions are not instantaneous.
Reason : Oppositely charged ions exert strong forces.

Answers

Electrical conductors, Arrenius theory and Ostwald's dilution law

1	c	2	b	3	b	4	b	5	b
6	a	7	b	8	d	9	a	10	a
11	c	12	d	13	b	14	b	15	d
16	d	17	b	18	b	19	c	20	c
21	a	22	c	23	b	24	d	25	c
26	d	27	a	28	d	29	d	30	c
31	b	32	c	33	c	34	c	35	a
36	c								

Acids and Bases

1	a	2	d	3	a	4	c	5	b
6	d	7	b	8	c	9	b	10	a
11	a	12	c	13	a	14	d	15	d
16	b	17	b	18	d	19	a	20	b
21	d	22	b	23	b	24	c	25	d
26	c	27	c	28	d	29	b	30	b
31	b	32	c	33	d	34	a	35	a
36	a	37	c	38	c	39	c	40	a
41	c	42	d	43	c	44	a	45	a
46	c	47	c	48	d	49	a	50	b
51	b	52	a	53	a	54	a	55	d
56	b	57	ab	58	a	59	c	60	d
61	a	62	b	63	b	64	b	65	a
66	a	67	d	68	a	69	a	70	b
71	b	72	d	73	b	74	d	75	b
76	b	77	a	78	a	79	b	80	a
81	d	82	b	83	b	84	d	85	bd
86	a	87	d	88	a	89	d	90	c
91	a	92	a	93	a	94	d	95	b
96	c	97	b	98	c	99	d	100	c
101	a	102	a	103	c	104	c	105	a
106	a	107	d	108	b	109	c	110	d
111	b	112	c	113	c	114	a	115	c

116	d	117	d	118	c	119	c	120	c
121	a	122	d	123	b	124	a	125	b
126	c	127	c	128	d	129	c	130	b
131	b	132	c	133	a	134	c	135	a
136	c	137	c	138	b	139	b	140	b
141	b	142	a	143	b	144	a	145	a
146	a	147	b	148	b	149	c	150	a
151	c	152	c	153	d	154	c	155	a
156	b	157	a	158	d	159	b	160	d
161	b	162	d	163	c	164	d	165	a

Common ion effect, Isohydric solutions, Solubility product, Ionic product of water and Salt hydrolysis

1	b	2	c	3	b	4	b	5	b
6	d	7	c	8	a	9	c	10	a
11	b	12	b	13	a	14	d	15	d
16	b	17	c	18	c	19	d	20	c
21	d	22	d	23	d	24	b	25	a
26	d	27	a	28	d	29	b	30	b
31	a	32	d	33	a	34	c	35	d
36	b	37	b	38	c	39	b	40	a
41	a	42	d	43	b	44	a	45	b
46	d	47	b	48	c	49	c	50	c
51	b	52	d	53	a	54	d	55	c
56	d	57	b	58	c	59	d	60	c
61	b	62	b	63	a	64	bc	65	d
66	a	67	d	68	a	69	d	70	c
71	c	72	d	73	d	74	d	75	a
76	c	77	b	78	d	79	b	80	d
81	c	82	c	83	d	84	c	85	d
86	d	87	b	88	c	89	b	90	a
91	a	92	a	93	c	94	c	95	a
96	d	97	d	98	b	99	b	100	ab
101	d	102	c	103	c	104	a	105	c
106	c	107	c	108	a	109	b	110	b
111	b	112	a	113	a	114	a	115	b
116	a								

Hydrogen ion concentration - *pH* scale and Buffer solution

1	a	2	c	3	d	4	b	5	b
6	d	7	a	8	c	9	b	10	d
11	a	12	d	13	c	14	a	15	b
16	d	17	b	18	c	19	c	20	d
21	b	22	c	23	a	24	d	25	b
26	a	27	a	28	d	29	b	30	b
31	d	32	b	33	a	34	a	35	c
36	c	37	c	38	a	39	a	40	d
41	a	42	a	43	b	44	d	45	b
46	a	47	b	48	a	49	c	50	a
51	a	52	c	53	c	54	c	55	d
56	a	57	c	58	b	59	b	60	c
61	b	62	c	63	b	64	b	65	c
66	a	67	b	68	d	69	a	70	c
71	d	72	a	73	b	74	a	75	b
76	a	77	a	78	c	79	b	80	a
81	b	82	c	83	b	84	b	85	c
86	b	87	a	88	a	89	a	90	d
91	b	92	c	93	a	94	a	95	c
96	b	97	b	98	b	99	b	100	b
101	c	102	c	103	a	104	a	105	c
106	a	107	c	108	c	109	d	110	b
111	d	112	d	113	b	114	a	115	c
116	d	117	b	118	b	119	d	120	c
121	d	122	b	123	c	124	d	125	b
126	b	127	a	128	c	129	b	130	d
131	c	132	d	133	c	134	c	135	a
136	c	137	c	138	c	139	c	140	b
141	b	142	a	143	d	144	b	145	b
146	d	147	c	148	b	149	a	150	d
151	b	152	d	153	b	154	b	155	c
156	d	157	c	158	a	159	c	160	d
161	c	162	d	163	b	164	a	165	d
166	a	167	d	168	b	169	c	170	a
171	c	172	c	173	d	174	b	175	a
176	c	177	a	178	c	179	a	180	b
181	c	182	b	183	b	184	b	185	c
186	b	187	b	188	a	189	a	190	b
191	d	192	b	193	b	194	b	195	a
196	b	197	b	198	b	199	a	200	ad
201	ac	202	a bc	203	c	204	c	205	b
206	b								

Critical Thinking Questions

1	b	2	a	3	b	4	a	5	d
6	a	7	c	8	a	9	a	10	a
11	b	12	d	13	c	14	d	15	c
16	d	17	d	18	b	19	b	20	d
21	a	22	b	23	a	24	b	25	a
26	c	27	d	28	d	29	b	30	d
31	b	32	a	33	c	34	a	35	a
36	b	37	c	38	b	39	a	40	b
41	a	42	a	43	a	44	a	45	a
46	c	47	b	48	b	49	b	50	c

51	d	52	c	53	b	54	c	55	a
56	d	57	d	58	c	59	a	60	a
61	a	62	c	63	d	64	b	65	a
66	a	67	b	68	b	69	d	70	b
71	a	72	c	73	a	74	c	75	c
76	a	77	b	78	a				

Assertion & Reason

1	c	2	b	3	a	4	a	5	a
6	c	7	c	8	a	9	e		

Answers and Solutions

Electrical conductors, Arrhenius theory and Ostwald's dilution law

1. (c) $C_{12}H_{22}O_{11}$ is a sugar and non-electrolyte.

2. (b) It is a weak electrolyte since it is slightly ionized.

3. (b) It is a weak electrolyte since slightly ionized.

4. (b) Because the degree of dissociation is inversely proportional to the concentration of the electrolyte.

5. (b) Electrolytes are those substances which on dissolving in water give ions.

6. (a)

$$K = \frac{\alpha^2 C}{1-\alpha}; \alpha = \frac{0.01}{100} \approx 1 \therefore K = \alpha^2 C = \left[\frac{0.01}{100}\right]$$

$$= 1 \times 10^{-8}.$$

7. (b) As $NaCl$ ionises completely to yield free ions.

8. (d) $CH_3COONa \rightleftharpoons CH_3COO^- + Na^+$

$H_2O \rightleftharpoons H^+ + OH^-$

$CH_3COOH + NaOH$

9. (a) $NaCl$, being a salt, is a strong electrolyte.

10. (a) We can determine by measurement of very dilute HF solutions.

11. (c) According to the Ostwald's dilution formula $\alpha^2 = \frac{K(1-\alpha)}{C}$. But for weak electrolytes α is very small. So that $(1-\alpha)$ can be neglected.

So that $\alpha = \sqrt{\frac{K_a}{C}}$.

12. (d) Arrhenius proposed the theory of ionisation.

13. (b) higher the dielectric constant of a solvent more of its ionising power.

14. (b) $\alpha \propto$ dilution of solution.

15. (d) Generally ionic compound are conduct electricity in fused state.

16. (d) According to Ostwald's dilution law because degree of ionization is directly proportional to the dilution.

17. (b) The degree of ionisation of a solute depends upon its nature, concentration, and temperature.

18. (b) Mathematical form of Ostwald's dilution law.

19. (c) It is a weak electrolyte because it's ionization is very less.

20. (c) When we add NH_4OH in NH_4Cl solution ionization of NH_4OH is decreased due to common ion effect.

21. (a) $BaCl_2 \rightleftharpoons Ba^{2+} + 2Cl^-$

Initially	1	0	0
After dissociation	$a-\alpha$	α	2α

Total = $1-\alpha+\alpha+2\alpha = 1+2\alpha$

$$\alpha = \frac{1.98-1}{\alpha} = \frac{0.98}{\alpha} = 0.49$$

for a mole $\alpha = 0.49$

For 0.01 mole $\alpha = \frac{0.49}{0.01} = 49$

22. (c) It is an ionic salt.

23. (b) Due to common ion effect of H^+.

24. (d) Current does not affect the degree of ionization.

25. (c) Polar solvent facilitate ionisation of strong electrolytes due to dipole-ion attraction.

26. (d) $HA \rightleftharpoons H^+ + A^-$

$K = Ca^2 = 0.1 \times (10^{-4})^2 = 10^{-9}$

28. (d) Degree of dissociation α = ?

Normality of solution = 0.1 N $= \frac{1}{10} N$

Volume = 10 *litre*

Dissociation constant $K = 1 \times 10^{-5}$

$K = \frac{\alpha^2}{V}$; $\alpha = \sqrt{KV}$ $= \sqrt{1 \times 10^{-5} \times 10}$;

$\alpha = 1 \times 10^{-2}$

29. (d) $MgCl_2 \rightleftharpoons Mg^{++} + 2Cl^-$ in aqueous solution it is dissociated into ions.

30. (c) Ostwald's dilution formula is $\alpha^2 = K(1-\alpha)/C$ but for weak electrolyte α is very small. So that $(1-\alpha)$ is neglected for weak electrolytes. So for weak electrolyte the dilution formula is $\alpha = \sqrt{\frac{K}{C}}$.

31. (b) $K_a = C\alpha^2 = 0.2 \times \left(\frac{32}{100}\right)^2 = 2.048 \times 10^{-4}$.

32. (c) $H_2SO_4 \rightleftharpoons H^+ + H^-SO_4 \rightleftharpoons H^+ + SO_4^{--}$

Because of it is completely ionised.

33. (c) Colour of electrolyte depends on the nature of both ions.

e.g. $CuSO_4$ is blue because Cu^{2+} ions are blue.

34. (c) Ionisation depends upon dilution, when dilution increases then ionisation is also increased.

35. (a) More is K_a, lesser is $pK_a\,(pK_a = -\log K_a)$ more is acidic strength.

Acids and Bases

1. (a) *CO* doesn't have a vacant *d*-orbital.

2. (d) $\underbrace{HClO_4 + H_2O \rightleftharpoons H_3O^+}_{\text{Conjugate acid and base pair}} + ClO_4^-$

3. (a) $FeCl_3 + 3H_2O \rightleftharpoons Fe(OH)_3 + 3HCl$. Strong acid and weak base.

4. (c) $Na_2CO_3 + 2H_2O \rightleftharpoons 2NaOH + H_2CO_3$

5. (b) Those substance accept the proton are called Bronsted base and which is donate the proton are called Bronsted acid.

$HCO_3^- + H^+ \rightleftharpoons H_2CO_3$ Bronsted base.

$HCO_3^- \rightleftharpoons H^+ + CO_3^{--}$ Bronsted acid.

7. (b) The value of pK_a for strong acid is less.

8. (c) Because it is a salt of strong base and weak acid.

9. (b) Because it is conjugate base of weak acid.

$CH_3COOH \rightleftharpoons CH_3COO^- + H^+$.

11. (a) Those compound which accept H^+ is called bronstad base NO_3^- accept H^+ and form HNO_3. So it is a base.

13. (a) Larger the size of halogen atom less is the back donation of electrons into empty 2*p* orbital of *B*.

14. (d) $H_2O + NH_3 \rightleftharpoons NH_4^+ + OH^-$

16. (b) $NH_2^- \rightleftharpoons NH^{-2} + H^+$

Conjugate acid, base pair.

17. (b) Those substances which lose proton are called acid.

e.g. strong acid have a strong tendency to donate a proton.

18. (d) Electron donating species called nucleophile. NH_3 have a lone pair of electron.

19. (a) H_2O acts as acid as it provides H^+ to NH_3.

20. (b) $CH_3COOH + HF \rightleftharpoons CH_3COOH_2^+ + F^-$. *HF* gives H^+ to the CH_3COOH. So it is a conjugate base of *HF*.

22. (b) $Ba(NO_3)_2$ does not undergo hydrolysis.

23. (b) H_2SO_4 is a mineral acid.

24. (c) Because it is a electron pair acceptor it's central atom have a vacant *d*-orbital.

25. (d) $HClO_4$ is a acid and their conjugate base is ClO_4^-.

26. (c) It is completely ionised because their ionization is very high.

27. (c) $NaHCO_3$ in water is alkaline in nature due to hydrolysis of HCO_3^- ion. $NaCO_3 \rightleftharpoons Na^+ + HCO_3^-$

28. (d) In this reaction H_2O acts as a acid.

29. (b) The basic character of hydride decreases down the group.

30. (b) Its ionization is very less.

32. (c) Hydrolysis of Cu^{2+} produces H^+ ions in solution.

$Cu^{2+} + 2H_2O \rightarrow Cu(OH)_2 + 2H^+$

33. (d) Both possess the tendancy to accept proton.

34. (a) *HF* does not give proton easily.

35. (a) In weak electrolyte the degree of dissociation is very small. So it increases with increasing dilution.

36. (a) Because it is a electron pair acceptor.

37. (c) $H_3PO_4 \xrightleftharpoons{\text{I step}} H^+ + H_2PO_4^-$

$H_2PO_4^- \xrightleftharpoons{\text{II step}} H^+ + HPO_4^{--}$

$HPO_4^{--} \xrightleftharpoons{\text{III step}} H^+ + PO_4^{---}$

38. (c) Na_2HPO_4 on hydrolysis of HPO_4^{2-} ion produces free OH^- ion in solution.

39. (c) $H_2SO_4 \rightleftharpoons H^+ + HSO_4^-$.

40. (a) $Fe^{3+} + 3H_2O \rightarrow Fe(OH)_3 + 3H^+$

41. (c) $\underset{\text{Conjugate acid}}{H_2PO_4^-} \rightleftharpoons H^+ + HPO_4^{2-}$ action.

42. (d) $H^+ + OH^- \rightleftharpoons H_2O$, it is a neutralization reaction.

43. (c) It is a conjugate base of the strong acid.

44. (a) Because those acid have higher pK_a value are weak acid.

45. (a) Conjugate acid is obtained from the base by gain of H^+.

46. (c) CH_3COOH is weak acid shows dissociation equilibrium as $CH_3COOH \rightleftharpoons CH_3COO^- + H^+$

47. (c) $pK_a = \log_{10}\frac{1}{K_a}$

48. (d) A weak acid and strong base.

49. (a) In NaH_2PO_2 both hydrogen are bonded with '*P*,' so it is not replaceable.

50. (b) Aqueous solution of Na_2CO_3 is alkaline due to hydrolysis of CO_3^{--}.

51. (b) Because they give CO_3^{--} in solution.

52. (a) M.eq. of 0.2*M* H_2SO_4 $= \frac{2 \times 0.2M}{1000} \times 100 = 0.04\ m/l$

M.eq. of .2*M* $NaOH = \frac{0.2}{1000} \times 100 = 0.02\ m/l$

left $[H^+] = .04 - .02 = .02$.

Total volume $= 200 = \frac{.02}{200} = .0001 = 10^{-4}\ M$

$pH = 4$.

53. (a) H_3BO_3 is a weak monobasic acid it does not act as a H^+ donor but behaves as a Lewis acid.

54. (a) Because $SnCl_2$ is a electron acceptor according to Lewis concept.

55. (d) *ROH* is a Lewis base because it has an lone pair of electron.

56. (b) $H_2SO_4 + 2H_2O \rightleftharpoons 2H_3O^+ + SO_4^{--}$

$NaOH \rightleftharpoons Na^+ + OH^-$

1 mole of H_2SO_4 acid gives 2 moles of H_3O^+ ions. So 2 moles of OH^- are required for complete neutralization.

57. (ab) Diprotic solvents give $2H^+$ ions or OH^- ions.

58. (a) $N_{NaOH} = 1 \times 1 = 1N$

$N_{H_2SO_4} = 2 \times 10 = 20N$

M.eq. of *NaOH* $= 1 \times 100 = 100$

M.eq. of $H_2SO4 = 20 \times 10 = 200$

Thus M.eq. of acid are left and therefore *pH*< 7, so the resulting mixture will be acidic.

60. (d) PH_3 is a Lewis base.

61. (a) Because of CH_3COONa is a salt of weak acid and strong base.

62. (b) Acid $\xrightarrow{-H^+}$ conjugate base.

Base $\xrightarrow{+H^+}$ conjugate acid.

63. (b) $\underset{\text{Acid}}{HCl} \rightarrow \underset{\text{Base}}{Cl^-}$

65. (a) $HClO_4 > \underset{\text{Aciedic character decreases}}{H_2SO_4 > HCl} > HNO_3$.

66. (a) Those substances which accept the H^+ are called conjugate base.

67. (d) NH_3 is a Lewis base, which donate a lone pair of electron.

69. (a) $FeCl_3 + 3H_2O \rightleftharpoons Fe(OH)_3 + 3HCl$. Strong acid have less than 7 *pH*.

70. (b) It donates their e^- pair.

71. (b) The strength of the acid will depend upon the proton donation.

73. (b) Because it is a salt of strong acid and strong base.

$$H^+_{(aq)} + Cl^-_{(aq)} + Na^+_{(aq)} + OH^-_{(aq)} \rightleftharpoons$$

$$H_2O_{(l)} + Na^+_{(aq)} + Cl^-$$

74. (d) CCl_4 is not a Lewis or bronsted acid. It does not contain H^+.

75. (b) $NH_4Cl + H_2O \rightleftharpoons \underset{\text{Weak base}}{NH_4OH} + \underset{\text{Strong acid}}{HCl}$. So it is acidic in nature.

76. (b) *Cu*(II) complexes are blue. The four water molecules are attached with secondary valencies of the metal atom e.g. $[Cu(H_2O)_4]SO_4 . H_2O$.

77. (a) The species which can accept as well as donate H^+ can act both as an acid and a base.

$\underset{\text{base}}{HSO_4^-} + H^+ \rightleftharpoons H_2SO_4$

$\underset{\text{acid}}{HSO_4^-} \rightleftharpoons SO_4^{2-} + H^+$

78. (a) NH_4^+ is the weakest acid. So its conjugate base is strongest.

79. (b) Ag^+ is an electron deficient compound and hence is a Lewis acid.

80. (a) $\underset{\text{Conjugate acid}}{H_3PO_4} \rightleftharpoons H^+ + H_2PO_4^-$

81. (d) $\underset{\text{Conjugate acid}}{HS_2O_8^-} \rightleftharpoons \underset{\text{Conjugate base}}{H^+ + S_2O_8^{--}}$

82. (b) PH_3 donates electron pair to BCl_3.

83. (b) The conjugate base of weak acid is a strong base.

84. (d) $OH^- \rightarrow \underset{\text{Conjugate base of } OH^-}{O^{2-} + H^+}$

85. (bd) Presence of lone pair of electron and they donate two electron pairs.

86. (a) *On increasing oxidation number Acidic strength increases.*

87. (d) H_3PO_4 is shows +5 maximum oxidation state.

88. (a) $C_2H_5^-$ is a strongest base.

89. (d) $NaOCl$ is a mixture of strong base and weak acid.

90. (c) NH_4OH gives minimum OH^- ion. So it is a weak base.

91. (a) Solution become acidic and methyl orange act on acidic *pH*.

92. (a) Larger is bond length, more is acidic nature (for halogen acids). *HF* bond length is small.

93. (a) HCl is accepting proton in *HF* medium and acts as weak base.

95. (b) For oxoacids of the same element, the acidic strength increases with increase in the oxidation number of that element.

$$\overset{+1}{HClO} < \overset{+3}{HClO_2} < \overset{+5}{HClO_3} < \overset{+7}{HClO_4}$$

96. (c) Because their conjugate base and conjugate acids are strong.

97. (b) *HCl* is a strong acid and their conjugate base is a very weak base.

100. (c) $NH_3 \rightleftharpoons NH_2^- + H^+$

101. (a) $H_2SO_4 \rightleftharpoons H^+ + HSO_4^- \rightleftharpoons H^+ + SO_4^{--}$

HSO_4^- is conjugate base. But it is also an acid because it lose H^+.

102. (a) BF_3 is a Lewis acid because '*B*' has incomplete octet.

104. (c) H_3O^+, however it exists as $H_9O_4^+$.

105. (a) $Al_2(SO_4)_3$ is a salt of weak base $Al_2(OH)_3$ and strong acid H_2SO_4.

106. (a) Al^{+++} of $AlCl_3$ undergoes hydrolysis.

107. (d) $H_2SO_4 \rightleftharpoons H^+ + HSO_4^-$

109. (c) Conjugate base of H_2SO_4 is HSO_4^-.

110. (d) Presence of lone pair.

111. (b) According to Bronsted principle HNO_3 is acid they give H^+ in aqueous solution and form NO_3^-.

112. (c) $H_2O + H_2O \rightleftharpoons H_3O^+ + OH^-$.

113. (c) NH_4^+ is a conjugate acid;

$NH_4^+ \rightleftharpoons NH_3 + H^+$

114. (a) $AlCl_3 + 3H_2O \rightleftharpoons Al(OH)_3 + \underset{\text{Stronacid}}{3HCl}$

116. (d) HCl is a strong acid its conjugate base means Cl^- is a weak base.

117. (d) Hydrazoic acid (HN_3) is a Lewis acid.

118. (c) Smaller the pK_a value than. Stronger the acid.

120. (c) BF_3 is acidic because due to Lewis concept it accept a lone pair of electron.

122. (d) Because it is a weak electrolyte.

126. (c) $AlCl_3$ and SO_2 both are example of Lewis theory.

127. (c) $Na_2CO_3 + 2H_2O \rightleftharpoons 2NaOH + H_2CO_3$. It is a strong base and weak acid so it is a basic.

129. (c) $\underset{\text{Acid}}{H_2O} + \underset{\text{base}}{NH_3} \rightleftharpoons NH_4^+ + OH^-$.

In this reaction H_2O acts as acid because it donate a proton.

130. (b) $\underbrace{H_2SO_4 + H_2O}_{\text{Conjugate acid and base pair}} \rightleftharpoons H_3O^+ + HSO_4^-$

131. (b) $Al_2(SO_4)_3 \rightleftharpoons 2Al^{3+} + 3SO_4^{2-}$

$\underset{\text{Weakbase}}{Al(OH)_3} + \underset{\text{Strongacid}}{H_2SO_4}$

132. (c) $NaOH + HCl \xrightarrow[\text{Reaction}]{\text{Neutralization}} \underset{\text{Salt}}{NaCl} + H_2O$

133. (a) Conjugate acid is obtained from the base by gain of H^+.

134. (c) KCl is a ionic compound .

135. (a) $H_3BO_3 + H_2O \rightleftharpoons [B(OH)_4]^- + H^+$

H_3BO_3 is a weak monobasic acid if does not act as a H^+ donor but behaves as a Lewis acid.

136. (c) Because it is not accept the proton.

137. (c) NH_4Cl is a salt of weak base (NH_4OH)and strong acid (*HCl*).

138. (b) Because it accept electron pair from the PH_3

139. (b) $NH_4^+ \rightleftharpoons NH_3 + H^+$

141. (b) Hydrolysis of Fe^{3+}

$Fe^{3+} + 3H_2O \rightarrow Fe(OH)_3 + 3H^+$

142. (a) According to the Lewis concept.

143. (b) Conjugate base is obtained from the acid by loss of H^+.

144. (a) BF_3 accept electron pair from NH_3 so it is Lewis acid.

145. (a) CH_4 has almost no acidic nature and thus CH_3^- is strongest base.

146. (a) $CuSO_4$ is a salt of weak base, $(Cu(OH)_2)$ and strong acid (H_2SO_4).

147. (b) Weak acid consists of highest pK_a value and strongest acid consist of less pK_a value.

149. (c) Because it gain and also lose the proton

$$H_2O + H_2O \rightleftharpoons H_3O^+ + OH^-$$

150. (a) $H_2O + H_2O \rightleftharpoons H_3O^+ + OH^-$

151. (c) $HBr + H_2O \rightleftharpoons H_3O^+ + Br^-$

152. (c) Because both are strong acid and strong base.

153. (d) $LiAlH_4$ is a nucleophilic and capable of donating electron pair, thus acts as a Lewis base.

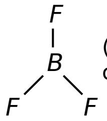
154. (c) The solvent which neither accept proton nor donates.

155. (a) Because of F^- is a highly electronegative. So it is easily lose the electron and reaction occur rapidly.

156. (b) Strong acid can be used titrate both strong and weak base.

159. (b) For a weak acid value of pKa will be vary high but in case of strong acid value of pKa will be vary low.

160. (d) Boron halides behave as Lewis acid because of their electron deficient nature *eg.*, as



(Deficiency of two electron for inert configuration)

161. (b) Gaseous *HCl* does not give H^+ but liquid *HCl* gives H^+ in aquous solution there for gaseous *HCl* is not a Arrhenius acid due to covalent bonding in gaseous condition.

162. (d) $\underset{\text{Acid}}{H_2O} \rightarrow H^+ + OH^-$ [Acid due to donation of proton]

$\underset{\text{Base}}{H_2O} + H^+ \rightarrow H_3O^+$ [Basic due to gaining of proton]

163. (c) F^- strongest conjugate base due to it smallest size in a group and gain proton due to most electronegative capacity.

$$H^+ + F^- \rightarrow HF$$

164. (d) $\underset{\text{Conjugate acid}}{H_2PO_4^-} \rightarrow H^+ + \underset{\text{Conjugate base}}{HPO_4^{2-}}$

165. (a) $\underset{\text{Conjugate acid}}{HSO_4^-} \rightarrow H^+ + \underset{\text{Conjugate base}}{SO_4^{2-}}$

Common ion effect, Isohydric solutions, Solubility product, Ionic product of water and Salt hydrolysis

1. (b) Solubility of $Al_2(SO_4)_3$

$$Al_2(SO_4)_3 \rightleftharpoons 2Al^{+++} + 3SO_4^{--}$$

$$K_{sp} = [Al^{3+}]^2 [SO_4^{2-}]^3$$

2. (c) Due to common ion effect.

3. (b) $MX_2 \rightleftharpoons \underset{S}{M^{2+}} + \underset{2S}{2X^-}$

$$K_{sp} = (2S)^2(S) = 4S^3$$

$$\Rightarrow S = 2\sqrt[3]{\frac{K_{sp}}{4}} = \sqrt[3]{\frac{4\times10^{-12}}{4}} = 1.0\times10^{-4}M.$$

5. (b) $MX_2 \rightleftharpoons \underset{(S)}{M^+} + \underset{(2S)^2}{2X^-}$; $K_{sp} = 4S^3$

$$S = \sqrt[3]{\frac{K_{sp}}{4}} = \sqrt[3]{\frac{1\times10^{-11}}{4}} = 1.35\times10^{-4}$$

8. (a) $Mg(OH)_2 \rightleftharpoons \underset{(X)}{Mg^{++}} + \underset{(2X)^2}{2OH^-}$

$$K_{sp} = 4X^3$$

9. (c) $BaSO_4 \rightleftharpoons \underset{\substack{(S)\\0.01}}{Ba^{++}} + \underset{\substack{(S)\\5}}{SO_4^{--}}$

$$K_{sp} = S^2 = S\times S = 0.01\times S$$

$$S_{(SO_4^{2-})} = \frac{K_{sp}}{S_{(Ba^{++})}} = \frac{1\times10^{-9}}{0.01} = 10^{-7}\ \textit{mole/litre}$$

10. (a) $AB_2 \rightleftharpoons \underset{1\times10^{-5}}{A^+} + \underset{2\times10^{-5}}{2B^-}$

$$K_{sp} = [1\times10^{-5}][2\times10^{-5}]^2 = 4\times10^{-15}$$

11. (b) $CaF_2 \rightleftharpoons \underset{(S)}{Ca^{++}} + \underset{(2S)^2}{2F^-}$; $K_{sp} = 4S^3$

12. (b) Due to common ion effect.

13. (a) $Ag_2CrO_4 \rightleftharpoons [2Ag^+] + [CrO_4^{--}]$

Hence $K_{sp} = [Ag^+]^2\ [CrO_4^{--}]$

14. (d) K_{sp} for $CaF_2 = 4s^3$

$$= 4\times[2\times10^{-4}]^3 = 3.2\times10^{-11}.$$

15. (d) The concentration of S^{2-} ions in group II is lowered by maintaining acidic medium in the presence of NH_4Cl. The ionization of H_2S is supressed due to common ion effect. So the ionic product is less than solubility product.

16. (b) NH_4Cl is hydrolysed and give $[H^+]$

$$NH_4Cl + H.OH \rightleftharpoons NH_4OH + HCl$$

$$NH_4^+ + H.OH \rightleftharpoons NH_4OH + H^+$$

17. (c) $FeCl_3$ is a salt of weak base $(Fe(OH)_3)$ and strong acid (*HCl*).

18. (c) For the precipitation of an electrolyte, it is necessary that the ionic product must exceed its solubility product.

19. (d) $K_{sp} = [Ag^+]^2[Cro_4^{--}] = [2S]^2[0.01]$

$= 4S^2[0.01] = 4[2\times10^{-8}]^2 \times 0.01$

$= 16\times10^{-18}$.

20. (c) Complex salts contain two different metallic elements but give test for only one of them. *e.g.* $K_4Fe(CN)_6$ does not give test for Fe^{3+} ions.

21. (d) $10^{-3}N$ *KOH* will give $[OH^-] = 10^{-2}M$

$pOH = 2$

$\because pH + pOH = 14$, $pH = 14 - 2 = 12$

22. (d) It is $FeSO_4(NH_4)_2SO_4 \,.\, 10H_2O$.

23. (d) Salt of a strong base with a weak acid.

24. (b) NH_4CN is a salt of weak acid and weak base and thus for it

25. (a) Because it is a salt of strong base with a weak acid.

26. (d) Because CCl_4 is a organic solvent and $AgNO_3$ is insoluble in organic solvent.

27. (a) $SnS_2 \rightleftharpoons Sn^{4+} + 2S^{2-}$

$\therefore K_{sp} = [Sn^{4+}]\,[S^{2-}]^2$

28. (d) It does not dissociate much or its ionization is very less.

29. (b) $NaHCO_3$ has one replaceable hydrogen.

30. (b) $CaOCl_2$ has two anions Cl^- and OCl^- along with Ca^{2+} ions.

31. (a) $K_{sp} = 4S^3$, $S^3 = \dfrac{4\times10^{-9}}{4} = 10^{-9}$

$\therefore S = 10^{-3}M$.

32. (d) $Be(OH)_2$ has lowest solubility and hence lowest solubility product.

33. (a) Because it is a salt of strong acid and strong base.

34. (c) $NH_4OH \rightleftharpoons \boxed{NH_4^+} + OH^-$

$NH_4Cl \rightleftharpoons NH_4^+ + Cl^-$ Common ion

35. (d) It is a less ionic, so that least soluble in water.

36. (b) *pH* of 9 means the salt solution should be fairly basic.

37. (b) $CH_3COOH \rightleftharpoons CH_3COO^- + H^+$

On adding CH_3COONa, $[H^+]$ decreases.

38. (c) 0.01 *M* $CaCl_2$ gives maximum Cl^- ions to keep K_{sp} of *AgCl* constant, decrease in $[Ag^+]$ will be maximum.

39. (b) Due to the common ion effect.

40. (a) $K_{sp} = 4s^3$

$$S = \sqrt[3]{\frac{K_{sp}}{4}} = \sqrt[3]{\frac{1.0\times10^{-6}}{4}} = 6.3\times10^{-3} .$$

42. (d) K_w increases with increase in temperature.

43. (b) It contains two cations and one anion.

44. (a) $HgSO_4$ of $K_{sp} = S^2$

$S = \sqrt{K_{sp}}$; $S = \sqrt{6.4\times10^{-5}}$; $S = 8\times10^{-3}$ *m/l.*

45. (b) The solubility of $BaSO_4$ in *g/litre* is given 2.33×10^{-3}

$\because$ in *mole/litre.* $n = \dfrac{W}{m.wt} = 1\times10^{-5}$

$= \dfrac{2.33\times10^{-3}}{233}$

Because $BaSO_4$ is a compound

$K_{sp} = S^2 = [1\times10^{-5}]^2 = 1\times10^{-10}$

46. (d) $\underset{a}{AgCl} \rightleftharpoons \underset{a}{Ag^+} + \underset{a}{Cl^-}$

$\underset{0.02}{NaCl} \rightleftharpoons \underset{0.02}{Na^+} + \underset{0.02}{Cl^-}$

$K_{sp}\ AgCl = 1.20\times10^{-10}$

$K_{sp}\ AgCl = [Ag^+][Cl^-] = a\times[a+0.2]$

$= a^2 + 0.2a$

a^2 is a very small so it is a neglected.

$K_{sp}\ AgCl = 0.2a$

$1.20\times10^{-10} = 0.2a$

$a = \dfrac{1.20\times10^{-10}}{0.20} = 6\times10^{-10}$ *mole*

47. (b) Solubility is decreased due to common ion effect.

$AgI \rightleftharpoons Ag^+ + \boxed{I^-}$ Common ion

$NaI \rightleftharpoons Na^+ + I^-$

48. (c) K_{sp} of $BaSO_4 = 1.5\times10^{-9}$; $Ba^{++} = 0.01M$

$SO_4^{--} = \dfrac{1.5\times10^{-9}}{0.01} = 1.5\times10^{-7}$

49. (c) $AgCrO_4 \rightleftharpoons \underset{(2S)^2}{2Ag^+} + \underset{S}{CrO_4^-}$

$K_{sp} = 4S^3$ given $2S = 1.5\times10^{-4}$

$\therefore K_{sp} = (2S)^2 \times S$

$= (1.5\times10^{-4})^2 \times \left(\frac{1.5\times10^{-4}}{2}\right)$

$= 1.6875\times10^{-12}$

50. (c) $PbCl_2 \rightleftharpoons \underset{S}{Pb^{2+}} + \underset{S}{2Cl^-}$

K_{sp} of $PbCl_2 = [Pb^{2+}]\times[Cl^-]^2$; $K_{sp} = S\times(2S)^2$

$K_{sp} = S\times 4S^2 = 4S^3$; $S^3 = \frac{K_{sp}}{4}$; $S = \sqrt[3]{\frac{K_{sp}}{4}}$

51. (b) $AgCl \rightleftharpoons [Ag^+][Cl^-]$; $K_{sp} = S\times S$; $K_{sp} = S^2$

$S = \sqrt{K_{sp}} = \sqrt{1.44\times10^{-4}} = 1.20\times10^{-2} M.$

52. (d) By formula $BA_2 \to B^+ + 2A^-$

$K_{sp} = 4x^3$

53. (a) $\underset{S}{AgCrO_4} \to \underset{2S}{2Ag^+} + \underset{S}{CrO_4^{--}}$

$K_{sp} = (2S)^2 S = 4S^3$

$S = \left(\frac{K_{sp}}{4}\right)^{\frac{1}{3}} = \left(\frac{32\times10^{-12}}{4}\right)^{\frac{1}{3}} = 2\times10^{-4} M.$

54. (d) Common ion effect is noticed only for weak electrolyte dissociation. H_2SO_4 is strong electrolyte.

55. (c) When we added barium ion in chromate ion solution we obtained yellow ppt of $BaCrO_4$.

$BaCl_2 + K_2CrO_4 \to \underset{\text{Yellow ppt.}}{BaCrO_4\downarrow} + 2KCl$

56. (d) *AB is a* binary electrolyte.

$S = \sqrt{K_{sp}} = \sqrt{1.21\times10^{-6}} = 1.1\times10^{-3} M$

57. (b) Precipitation occurs when ionic product > solubility.

58. (c) For a binary electrolyte, so that

$K_{sp} = S\times S = S^2$

$S = \sqrt{K_{sp}}$.

61. (b) CH_3COONa is a salt of weak acid and strong base. Hence its aqueous solution is alkaline.

62. (b) $BaSO_4 \rightleftharpoons Ba^{2+} + SO_4^{--}$

Solubility constant $= S\times S$

$1.5\times10^{-19} = S^2$; $S = \sqrt{1.5\times10^{-19}}$;

$S = 3.9\times10^{-5}$

65. (d) $Ca(OH)_2 \rightleftharpoons \underset{(S)}{Ca^{++}} + \underset{(2S)^2}{2OH^-}$

$K_{sp} = 4S^3 = 4\times\sqrt{3}\times\sqrt{3}\times\sqrt{3} = 12\sqrt{3}$

66. (a) Due to common ion effect.

67. (d) $PbCl_2 \rightleftharpoons \underset{(S)}{Pb^{2+}} + \underset{(2S)^2}{2Cl^-}$

$K_{sp} = 4S^3 = 4\times(2\times10^{-2})^3 = 3.2\times10^{-5}$

68. (a) $Ag_2S \rightleftharpoons 2Ag^+ + S^{--}$

$K_{sp} = 4S^3$

$S = \sqrt[3]{\frac{K_{sp}}{4}} = \sqrt[3]{\frac{3.2\times10^{-11}}{4}} = 2\times10^{-6}$

69. (d) $\underset{S}{CaCO_3} \rightleftharpoons \underset{S}{Ca^{++}} + \underset{S}{CO_3^{--}}$

Solubility product of $CaCO_3$

$K_{sp} = S^2$; $S = \sqrt{K_{sp}}$

It is a binary electrolyte.

$S^2 = K_{sp}$; $(3.05\times10^{-4})^2 = K_{sp}$;

$K_{sp} = 9.3\times10^{-8}$

71. (c) $PbCl_2 \to \underset{S}{Pb^{++}} + \underset{2S}{2Cl^-}$

$K_{sp} = S\times(2S)^2$

$= [6.3\times10^{-3}]\times[12.6\times10^{-3}]^2$.

72. (d) A salt of strong acid and strong base cannot be hydrolysed. In this case the equilibrium cannot shifted towards the backward.

73. (d) If we mixed any substance into the solution. Then the value of *pH* is increased these substance is a salt of weak acid and strong base.

74. (d) It is a salt of strong base and weak acid.

75. (a) $K_{sp} = 4s^3 = 4\times[2.5\times10^{-2}]^3 = 62.5\times10^{-6}$.

76. (c) $NaCl \rightleftharpoons \underset{S}{Na^+} + \underset{S}{Cl^-}$

$K_{sp} = S^2$, $S = \sqrt{K_{sp}} = \sqrt{36} = 6$.

78. (d) $\underset{K_{sp}}{PbI_2} \rightleftharpoons \underset{S}{Pb^{++}} + \underset{2S}{2I^-}$

$K_{sp} = 4S^3 = 4\times[2\times10^{-3}]^3 = 32\times10^{-9}$.

79. (b) When ionic product is greater than K_{sp} then precipitation occur

$K_{sp} < 10^{-2} M\ Ca^{2+} + 10^{-3} M\ F^-$

80. (d) In IVth group the S^{2-} concentration increase when added the NH_4OH becaus

$NH_4OH \rightleftharpoons NH_4^+ + OH^-$

$H_2S \rightleftharpoons 2H^+ + S^{2-}$

$OH^- + H^+ \rightleftharpoons H_2O$. So that S^{2-} is increased.

81. (c) $BaSO_4 \rightleftharpoons Ba^{2+} + SO_4^{2-}$

$K_{sp} = S^2 \Rightarrow S = \sqrt{K_{sp}}$; $K_{sp} = [Ba^{2+}] \times [SO_4^{2-}]$

$4 \times 10^{-10} = [1 \times 10^{-4}] \times [SO_4^{2-}]$

$[SO_4^{2-}] = \frac{4 \times 10^{-10}}{1 \times 10^{-4}} = 4 \times 10^{-6}$.

82. (c) $AB_2 \rightleftharpoons \underset{(S)}{A^{2+}} + \underset{(2S)^2}{2B^-}$

$K_{sp} = 4S^3$

$S = \sqrt[3]{\frac{K_{sp}}{4}} = \sqrt[3]{\frac{4 \times 10^{-12}}{4}}$

$= 1 \times 10^{-4}$ $gmmol/litre$

83. (d) $[B] = \frac{K_{sp}AB}{[A]} = \frac{1 \times 10^{-8}}{10^{-3}} = 1 \times 10^{-5} M$

Where ionic product > K_{sp}, ppt formed

$\therefore$ 8 should be more then $10^{-5} M$.

84. (c) $NaCl_{(s)} \rightleftharpoons Na^+_{(aq)} + Cl^-_{(aq)}$

$HCl \rightleftharpoons H^+ + Cl^-$. The increase in $[Cl^-]$ brings in an increase in $[Na^+][Cl^-]$ which will lead for backward reaction because

$K_{sp}(NaCl) = [Na^+][Cl^-]$

means Ionic product $\geq K_{sp}$

85. (d) $BaSO_4 \rightleftharpoons \underset{(S)}{Ba^{++}} + \underset{(S)}{SO_4^{--}}$

$K_{sp} = S^2$; $S = \sqrt{K_{sp}} = \sqrt{1.3 \times 10^{-9}}$

$= 3.6 \times 10^{-5}$ $mol/litre$

87. (b) Alkaline,

$CH_3COONa + H_2O \rightleftharpoons \underset{\text{Weak acid}}{CH_3COOH} + \underset{\text{Strong base}}{NaOH}$

88. (c) Because it is a strong base.

89. (b) For pure water $[H^+] = [OH^-]$, $\therefore K_w = 10^{-12}$s

90. (a) $MX_2 \rightleftharpoons \underset{(S)}{M^{2+}} + \underset{(2S)^2}{2X^-}$;

$4S^3 = 4 \times (0.5 \times 10^{-4})^3$

$= 5 \times 10^{-13}$

91. (a) Solubility coefficient $= [Pb^{2+}][Cl^-]^2$

92. (a) Solubility of $Al(OH)_3$ is lesser than $Zn(OH)_2$.

93. (c) $NaCl_{(s)} \rightleftharpoons Na^+_{(aq)} + Cl^-_{(aq)}$

$HCl \rightleftharpoons H^+ + Cl^-$

The increase in $[Cl^-]$ brings in an increase in $[Na^+][Cl^-]$ which will lead for backward reaction because $K_{sp}\,NaCl = [Na^+][Cl^-]$.

94. (c) Common ion effect.

95. (a) $\underset{S}{CaF_2} \rightleftharpoons \underset{S}{Ca^{++}} + \underset{(2S)^2}{2F^-}$

$K_{sp} = 4S^3$

$S = \sqrt[3]{\frac{K_{sp}}{4}} = \sqrt[3]{\frac{3.2 \times 10^{-11}}{4}} = 2 \times 10^{-4}\ m/l.$

96. (d) In aqueous solution following euilibrium is exist. $H_2S \rightleftharpoons H^+ + HS^-$

While adding the dilute HCl solution

$(HCl \rightleftharpoons H^+ + Cl^-)$ equilibrium is shift to the left side in $H_2S \rightleftharpoons H^+ + HS^-$

97. (d) $\underset{K_{sp}}{M_2X_3} \rightleftharpoons \underset{(2y)^2}{2M^{+++}} + \underset{(3y)^3}{3X^{--}}$

Solubility product $K_{sp} = 108y^5\ mol\frac{d}{m^3}$

98. (b) Solubility is directly proportional to the K_{sp}.

99. (b) $\underset{S}{PbCl_2} \rightleftharpoons \underset{S}{Pb^{++}} + \underset{(2S)^2}{2Cl^-}$

$K_{sp} = S \times (2S)^2 = 4S^3$

$S = \sqrt[3]{\frac{K_{sp}}{4}} = \sqrt[3]{\frac{1.5 \times 10^{-4}}{4}} = 3.34 \times 10^{-2}$.

101. (d) $AlCl_3$ on hydrolysis gives weak base and strong acid among all.

102. (c) Fe^{3+} ions are hydrolysed to develop acidic nature.

103. (c) $K_h = \frac{K_w}{K_a \times K_b}$

104. (a) KCN is salt of strong base and weak acid.

105. (c) Sulphides of Group-II radicals have low solubility product.

106. (c) Because NH_3 acts as Lewis acid and they give electron pair to H_3O^+ ion. H_3O^+ is a Lewis base. Which accept the electron pair from NH_3.

107. (c) Due to common ion effect.

108. (a) For $Ag_2SO_4 \rightarrow \underset{2x}{2Ag^+} + \underset{x}{SO_4^{--}}$

$K_{sp} = (2x)^2.x$; $K_{sp} = 4x^3$;

$K_{sp} = 4 \times (2.5 \times 10^{-2})^3$

$K_{sp} = 62.5 \times 10^{-6}$

109. (b) For $AgCl \rightarrow \underset{x}{Ag^+} + \underset{x}{Cl^-}$

$K_{sp} = x^2$; $x = \sqrt{K_{sp}}$,

$\sqrt{1 \times 10^{-6}} = 1 \times 10^{-3}\, mole/litre$.

110. (b) $AgCl \rightarrow \underset{x}{Ag^+} + \underset{x}{Cl^-}$

After *NaCl* is added x $\quad x + 1 \times 10^{-4}$

That is why Ag^+ will be less.

111. (b) Because of ionic product of $AgI >>$ solubility product of its.

112. (a) $AX_2 \rightarrow \underset{x}{A} + \underset{2x}{2X}$

$K_{sp} = 4x^3$; $x = \sqrt[3]{\frac{3.2 \times 10^{-11}}{4}}$; $x = 2 \times 10^{-4}$ *mole/litre.*

113. (c) $C_6H_5COONH_4 \rightarrow C_6H_5COO^- + NH_4^+$

$0.5 - \frac{.25}{100} \quad \frac{.25}{100} \quad \frac{.25}{100}$

According to Ostwald dilution law.

$$K = \frac{\alpha^2 C}{1-\alpha}$$

$$\left(\therefore\ \alpha = \frac{.25}{100}\right)$$

$K = \alpha^2 C \qquad (\because\ 1-\alpha = \text{Very small})$

$K = \frac{.25}{100} \times \frac{.25}{100} \times .5$; $K = 3.125 \times 10^{-6}$

114. (a) $Sb_2S_3 \rightarrow \underset{2x}{2Sb^{+2}} + \underset{3x}{3S^{--}}$; $K_{sp} = (2x)^2.(3x)^3$

$K_{sp} = 108x^5$; $K_{sp} = 108 \times (1 \times 10^{-5})^5$

$= 108 \times 10^{-25}$.

115. (b) When increasing the temperature the value of ionic product also increases.

116. (a) Hydrolysis constant $h = \frac{K_w}{K_a}$

Hydrogen ion concentration - *p*H scale and Buffer solution

1. (a) *pH* of blood does not change because it is a buffer solution.

2. (c) 0.001 *M* of $NaOH$ means $[OH^-] = .001$

$= 10^{-3} M \Rightarrow pOH = 3$

$pH + pOH = 14 \Rightarrow pH = 14 - 3 = 11$

3. (d) $[H_3O^+]$ means $[H^+] = 6.2 \times 10^{-9}\ mol/l$

$pH = -\log(6.2 \times 10^{-9}) = 8.21$

4. (b) $CH_3NH_2 + HCl \rightarrow CH_3NH_3^+Cl^-$

0.1 0.08 0

0.02 0 0.08

(Basic buffer solution)

$pOH = pK_b + \log \frac{0.08}{0.02}$

$= pK_b + 0.602$

$= 3.30 + 0.602 = 3.902$

$\therefore pH = 10.09$

$[H^+] = 7.99 \times 10^{-11} \approx 8 \times 10^{-11}\ M$

5. (b) $pH + pOH = pK_w$

6. (d) $pH = -\log[H^+]$

$5.4 = -\log[H^+]$; $[H^+] = 3.98 \times 10^{-6}$.

7. (a) $KCN + H_2O \rightleftharpoons KOH + HCN$. KOH is a strong base and HCN is a weak acid.

8. (c) $[H^+] = 10^{-3} M$, $pH = -\log[10^{-3}]$, $pH = 3$

9. (b) $[H^+] = [OH^-]$

$K_w = [H^+][OH^-] = 10^{-14}$

$\therefore [H^+] = 10^{-7}$, $pH = -\log[H^+] = 7$.

10. (d) $pH = 5$ means $[H^+] = 10^{-5}$

$pOH = 14 - pH = 14 - 5 = 9$

$[OH^-] = 10^{-pOH} = 10^{-9}$

11. (a) $pH = -\log[H^+]$; $[H^+] = 0.01N$

$pH = -\log[10^{-2}]$; $pH = 2$

12. (d) $BOH \rightleftharpoons B^+ + OH^-$

Initial $C \quad 0 \quad 0$

At eq. $C - C\alpha \quad C\alpha \quad C\alpha$

$K_b = \frac{C^2\alpha^2}{C(1-\alpha)} = C\alpha^2$ assuming $\alpha << 1$; $1 - \alpha \simeq 1$

$10^{-12} = 10^{-2} \times \alpha^2$; $\alpha^2 = 10^{-10}$; $\alpha = 10^{-5}$

$[OH^-] = C\alpha = .01 \times 10^{-5} = 10^{-7}$

13. (c) $pH = 4$ means; $[H^+] = 10^{-4}\ mol$

14. (a) Buffer solution is a mixture of weak acid and its conjugate base.

15. (b) Adding Na_2CO_3 to water makes the solution basic and hence a *pH* increases from 7.

16. (d) $NaClO_4$ is a salt of strong acid $HClO_4$. So it is a strong acid salt.

17. (b) $NaOH$ is a base, so that its $pH > 7$

18. (c) It is a strong base.

1 M $NaOH$ has maximum $[OH^-]$ and minimum $[H^+]$ and maximum pH.

19. (c) When pH = 7 means neutral, pH < 7 means acidic, pH > 7 means basic.

20. (d) As the solution is acidic, $pH < 7$. This is because $[H^+]$ from $H_2O[10^{-7}M]$ cannot be neglected in comparison to 10^{-10} M

22. (c) It is a strong acid and they lose proton in a solution.

23. (a) $[OH^-] = 10^{-2}M$; $pOH = 2$

$pH + pOH = 14$; $pH = 14 - pOH$

$pH = 14 - 2 = 12$

24. (d) Order of acidic strength is $H_2Te > H_2Se > H_2S > H_2O$

Na_2O is a salt of NaOH $+H_2O$ and H_2O is least acidic among given acids hence pH in this case will be max^m.

25. (b) pH of the solution A = 3

$[H^+]_A = 10^{-3}$ M.

pH of the solution B = 2

$[H^+]_B = 10^{-2}$ M

$[H^+] = 10^{-3} + 10^{-2} = 10^{-3} + 10 \times 10^{-3} = 11 \times 10^{-3}$.

$pH = -\log(11 \times 10^{-3}) = 3 - \log 11$

$= 3 - 1.04 = 1.95$

26. (a) $CN^- + H_2O \rightarrow HCN + OH^-$

Because OH^- concentration is increased.

27. (a) On dilution the pH of acid A increases while pH of base B decreases.

28. (d) CH_3COONa is a salt of weak acid, (CH_3COOH) and strong base $(NaOH)$.

29. (b) The equilibrium will shift in the backward direction.

30. (b) $K_a = 10^{-5}$; $pH = 6$

$$pH = -\log K_a + \log\frac{[\text{Salt}]}{[\text{Acid}]};$$

$$6 = -\log 10^{-5} + \log\frac{[\text{Salt}]}{[\text{Acid}]}$$

$$6 = 5\log 10 + \log\frac{[\text{Salt}]}{[\text{Acid}]};\ 6 = 5 + \log\frac{[\text{Salt}]}{[\text{Acid}]}$$

$$\log\frac{[\text{Salt}]}{[\text{Acid}]} = 6 - 5 = 1;\ \frac{[\text{Salt}]}{[\text{Acid}]} = \frac{10}{1}$$

31. (d) All are true – (a) is true for acid buffer, (b) for basic buffer, (c) is called buffer solution.

32. (b) $\frac{N}{100} = 0.01N\ HCl$; $[H^+] = 10^{-2}M$; $pH = 2$

$[OH] = 10^{-2}M$ for $NaOH$

$pH + pOH = 14$; $pH = 14 - 2$; $pH = 12$

34. (a) It is a buffer solution of strong acid and its weak conjugate base.

35. (c) $HA \rightleftharpoons H^+ + A^-$

$[H^+] = 0.1\ M$; $[H^+]^2 = K_a \times C$

$[H^+] = \sqrt{K_a \times C} = \sqrt{1 \times 10^{-5} \times 0.1} = \sqrt{10^{-6}}$

$[H^+] = 10^{-3}M$; $pH = 3$

36. (c) As the solution is acidic, $pH < 7$. This is because $[H^+]$ from H_2O cannot be neglected in comparison to 10^{-8}.

37. (c) Human body contain buffer solution. Its pH= 6.8

38. (a) It is a neutral solution and its pH = 7

39. (a) $pH = 5$, means $[H^+] = 10^{-5}M$.

After dilution $[H^+] = 10^{-5}/100 = 10^{-7}M$

$[H^+]$ from H_2O cannot be neglected.

Total $[H^+] = 10^{-7} + 10^{-7} = 2 \times 10^{-7}$

$pH = 7 - 0.3010 = 6.6990 = 7$ (neutral).

40. (d) $[H^+] = \alpha.C = \frac{2}{100} \times .02$; $[H^+] = 4 \times 10^{-4}\ M$

$pH = -\log[H^+] = 4 - \log 4$; $pH = 3.3979$

41. (a) $pH = pK_a + \log\left[\frac{\text{salt}}{\text{acid}}\right]$

$= 9.30 + \log\left[\frac{0.2}{0.1}\right] = 9.30 + 0.3010 = 9.6.$

42. (a) $pH = pK_a + \log\frac{[\text{Salt}]}{[\text{Acid}]}$

$pH = -\log(1.8 \times 10^{-5}) + \log\frac{[10]}{[100]}$

$= -\log 1.8 + 5 + \log 10^{-1}$

$= -0.2553 + 5 - 1 = 3.7447$ or $= 4$

43. (b) 20 ml. of 0.1 $NHCl$ = $\frac{0.1}{1000} \times 20g$ eq. = $2 \times 10^{-3}g$ eq.

20ml. of 0.001 KOH = $\frac{0.001}{1000} \times 20gm$eq.

= 2 × $10^{-5}g$ eq.

$\therefore$ HCl left unneutralised = $2(10^{-3} - 10^{-5})$

$= 2 \times 10^{-3}(1 - 0.01)$ = $2 \times 0.99 \times 10^{-3}$ $= 1.98 \times 10^{-3} geq$

Volume of solution = 40 ml.

$\therefore$ $[HCl]$ = $\frac{1.98\times10^{-3}}{40}\times1000M$ = 4.95×10^{-2}

$\therefore$ pH = $2-$ log 4.95 = 2 – 0.7 = 1.3.

45. (b) $10^{-7}M$ $NaOH$ means $[OH^-]=10^{-7}$; $pOH=7$ $pH=14-7=7$

46. (a) $[H^+]=c\times\alpha=0.1\times\frac{30}{100}=0.03M$

48. (a) The pH of buffer solution never changed.

49. (c) $[H^+]=\frac{10^{-14}}{10^{-1}}=10^{-13}$ $mol/litre$ $pH=13$.

50. (a) $pH=-\log[H^+]$; $7.4=-\log[H^+]$; $[H^+]=4\times10^{-8}M$

51. (a) The pH of 0.1M $HCl=1$ Ionization of H_2SO_4 takes place in two steps.

$H_2SO_4\rightleftharpoons H^++HSO_4^-$; $HSO_4^-\rightleftharpoons H^++SO_4^{--}$

52. (c) 1N $NaOH$ solution have highest pH

$[OH^-]=1$; $pOH=0$; $pH+pOH=14$

$pH=14-0=14$

53. (c) $H_2O\rightleftharpoons[H^+][OH^-]$

$HCl\rightleftharpoons[H^+][Cl^-]$

Total $[H^+]=[H^+]_{H_2O}+[H^+]_{HCl}$

$=10^{-7}+10^{-8}$

$=10^{-7}[1+10^{-1}]$

$[H^+]=10^{-7}\times\frac{11}{10}$

$pH=-\log[H^+]=-\log\left(10^{-7}+\frac{11}{10}\right)$;

$pH=6.958$

54. (c) pK_a = – log K_u, pK_b = – log K_b

pH = $-\frac{1}{2}[\log K_a+\log K_w-\log K_b]$

$=-\frac{1}{2}[-5+\log(1\times10^{-14})-(-5)]$

$=-\frac{1}{2}[-5-14+5]=-\frac{1}{2}(-14)=7$

55. (d) BaO, CaO and Na_2O are shows more than 7 pH because of their basic nature.

56. (a) $MgCl_2+2H_2O\rightleftharpoons Mg(OH)_2+2HCl$

57. (c) H_2SO_4 ionized in two step.

58. (b) $pH=pK_a+\log\frac{[\text{Salt}]}{[\text{Acid}]}$

$5.8=4.8+\log\frac{[\text{Salt}]}{[\text{Acid}]}$ or $\log\frac{[\text{Salt}]}{[\text{Acid}]}=1.0$

$\frac{[\text{Salt}]}{[\text{Acid}]}=\text{antilog}\,1.0=10$

$\therefore$ $\frac{[\text{Acid}]}{[\text{Salt}]}=\frac{1}{10}=0.1$

59. (b) It contains replacable H atom.

60. (c) (i) 20 ml of 0.5 N HCl

$0.5N\Rightarrow 1000ml/0.5\,mole\,HCl$ is present in $20ml$

$=\frac{20\times0.5}{1000}=1.0\times10^{-2}$

(ii) 35 ml of 0.1 N $NaOH$

$0.1N\Rightarrow1000ml$ of 0.1 mole $NaOH$ is 35 ml

$=\frac{35\times0.1}{1000}=0.35\times10^{-2}$

Total = 20 + 35 = 55 ml.

⇒ $(1.0–0.35)10^{-2}=0.65\times10^{-2}$mole HCl

$HCl = H^++Cl^-$

⇒ $[HCl] = [H^+]+[Cl^-]$

55 ml contains 0.65×10^{-2} mole of H^+ ions

$1000ml-\frac{0.65\times10^{-2}\times10^{3}}{55}=\frac{6.5}{55}$

$pH=-\log[H^+]=-\log(6.5/55)$

$=\log55-\log6.5=0.92$

Due to acidic nature of solutions the colour of phenolphthalein becomes pink.

61. (b) $[H^+]=2\times10^{-2}M$

$\because$ $pH=-\log[2\times10^{-2}]$;

$pH=1.7$ *i.e.* in between 1 and 2.

63. (b) $pH=4$, $(H^+)=10^{-pH}=10^{-4}M$

65. (c) $NaOH\rightleftharpoons Na^++OH^-$

$[OH^-]=10^{-5}M$; $[H^+][OH^-]=10^{-14}$

$[H^+]=\frac{10^{-14}}{10^{-5}}$; $[H^+]=10^{-9}M$; $pH=9$.

67. (b) $pH=pK_a+\log\frac{[\text{Salt}]}{[\text{Acid}]}$;

$pH=4.75+\log\frac{0.1}{0.1}$

$pH=4.75+\log1$; $pH=4.75$

68. (d) A weak acid and its salt with a strong base maintain pH 4 – 5

69. (a) $NaOH\rightleftharpoons Na^++OH^-=[OH^-]=10^{-8}M$.

70. (c) $[OH^-]=0.0001N$, $pOH=4$, $pH+pOH=14$

$pH=14-pOH=14-4=10$

71. (d) 0.001 *M KOH* solution

$[OH^-]=0.001M=1\times10^{-3}M$

$[H^+]\times[OH^-]=1\times10^{-14}$

$$[H^+]=\frac{1\times10^{-14}}{[OH^-]}$$

$$[H^+]=\frac{1\times10^{-14}}{1\times10^{-3}}=1\times10^{-14}\times10^{+3}$$

$[H^+]=10^{-11}M$

$pH=11$

72. (a) An acid buffer solution consists of solution of weak acid with strong base of its salt.

73. (b) An acid buffer solution consists of a weak acid and its salt with strong base. *i.e.* $CH_3COOH+CH_3COONa$

74. (a) $pOH=pK_b+\log\frac{[salt]}{[base]}$

$$=5+\log\frac{0.02}{0.2}=5+\log\frac{1}{10}=5+(-1)=4$$

$pH=14-pOH=14-4=10$

75. (b) [Salt]= 0.1 *M*, [Acid]= 0.1 *M*

$K_a=1.8\times10^{-5}$;

$$pH=-\log K_a+\log\frac{[Salt]}{[Acid]}$$

$$=-\log 1.8\times10^{-5}+\log\frac{0.1}{0.1}$$

$=-\log 1.8\times10^{-5}$

$pH=4.7$.

76. (a) NH_4Cl and NH_4OH is a buffer solution (weak base and salt of strong acid).

77. (a) $pH+pOH=14$; $pH=14-pOH$

$\because [OH^-]=10^{-7}$

$pOH=7$

$\therefore pH=14-7=7$.

78. (c) 0.01 *M* $Ba(OH)_2=0.02N\ Ba(OH)_2$

$N_1V_1=N_2V_2$

$[0.02N]\times[50\,ml]=N_2\times100\,ml$

$$N_2=\frac{0.02\times50}{100}=10^{-2}N\ ;\ [OH^-]=10^{-2}N$$

$pOH=2$ or $pH=12$

79. (b) $pH=-\log[H^+]$.

80. (a) Na_2CO_3 is a mixture of weak acid and strong base, so it is a base.

81. (b) $10^{-7}N\ HCl$ means $(H^+)=10^{-7}M$

$pH=-\log(H^+)$, $pH=7$

82. (c) $pH=2$; $pH=-\log[H^+]$; $2=-\log[H^+]$

$[H^+]=10^{-2}=0.01N$

83. (b) *pH* does not change on addition of some concentration of *HCl*.

84. (b) Solution of CH_3COONa on addition to acid shows a decrease in dissociation of acid due to common ion effect. To decrease in $[H^+]$ or increase *pH*.

85. (c) $pH+pOH=14$; $pH=14-pOH$; $pH=14-6=8$.

86. (b) $[H^+]_I=10^{-5}$ $[H^+]_{II}=10^{-2}$

Thus increase in $[H^+]=\frac{10^{-2}}{10^{-5}}=1000$ times

87. (a) The *HCl* is a strong acid and they lose easily H^+ in solution.

88. (a) $X^-+H_2O\rightleftharpoons OH^-+HX$

$$K_b=\frac{[OH^-][HX]}{[X^-]}$$

$HX\rightleftharpoons H^++X^-$

$$K_a=\frac{[H^+][X^-]}{[HX]}$$

$\therefore K_a\times K_b=[H^+][OH^-]=K_w=10^{-14}$

Hence $K_a=10^{-4}$

Now as $[X^-]=[HX]$, $pH=pK_a=4$.

90. (d) Buffer solution is formed. So the *pH* will not change.

91. (b) Na_2CO_3 when react with water form strong base and weak acid. So its aqueous solution is basic.

92. (c) $K_w=[H_3O^+][OH^-]$

Concentration of H_3O^+ in distilled water $=1\times10^{-6}$ *mol/l*.

Now $[H_3O^+]=[OH^-]$

$K_w=[1\times10^{-6}]\times[1\times10^{-6}]=1\times10^{-12}$.

93. (a) $[OH^-]=10^{-1}M$; $pOH=1$

$pH+pOH=14$; $pH=14-1=13$.

94. (a) Maximum *pH HClO* is a weak acid all of these. So that the salt of weak acid is also weak.

95. (c) As the solution is acidic $pH < 7$. This is because $[H^+]$ from H_2O $[10^{-7}]$ cannot be neglected in comparison to $10^{-12} M$.

96. (b) [Normal salt + acidic salt] is a buffer solution.

97. (b) 100 *ml* of $\frac{M}{10} NaOH$ = 50*ml* of $\frac{M}{5} NaOH$. They exactly neutralise 50 *ml* $\frac{N}{5} HCl$. Hence *pH* of resulting solution = 7.

98. (b) $M_1 = 6.0 M$ of HCl ; $V_1 = ?$

M_2 =0.30 *M* is H^+ concentration in solution.

V_2 =150 *ml* of solution.

$$M_1V_1 = M_2V_2 ;\ 6.0 \times V_1 = .30 \times 150$$

$$V_1 = \frac{.30 \times 150}{6} = 7.5\ ml.$$

99. (b) $pH = 3,\ [H^+] = 10^{-3} M$

$$\because [H^+] = \sqrt{K \times c}$$

$$[10^{-3}]^2 = K \times c\ ;\ \frac{[10^{-6}]}{0.1} = K = 10^{-5}$$

100. (b) When ratio of concentration of acid to salt is increased *pH* decrease.

101. (c) For NH_4OH .

$$[OH^-] = C.\alpha\ ;\ C = \frac{1}{10} M,\ \alpha = 0.2$$

$$[OH^-] = \frac{1}{10} \times 0.2 = 2 \times 10^{-2} M$$

$$pOH = -\log[OH^-] = \log[2 \times 10^{-2}];$$

$$pOH = 1.7$$

$$pH = 14 - pOH = 14 - 1.7 = 12.30.$$

102. (c) $pH = pK_a + \log\frac{[\text{Salt}]}{[\text{Acid}]}$. For small concentration of buffering agent and for maximum buffer capacity $\frac{[\text{Salt}]}{[\text{Acid}]} \approx 1$.

103. (a) $[H^+]$= increased ten fold means *pH* of solution decreased by one.

$$pH = \log\frac{1}{[H^+]}$$

104. (a) Because the *pH* of buffer are not changed.

105. (c) $pH = pK_a + \log\frac{[\text{Salt}]}{[\text{Acid}]}$;

$$5.5 = 4.5 + \log\frac{[\text{Salt}]}{[0.1]}$$

$$\log\frac{[\text{Salt}]}{0.1} = 5.5 - 4.5 = 1$$

$\frac{[\text{Salt}]}{0.1}$ =antilog 1 = 10 ; $[\text{Salt}] = 1$

106. (a) Moles of $H_2SO_4 = \frac{0.49}{98} = 5 \times 10^{-3}$ moles of H_2SO_4 present per litre of solution (molarity) $= \frac{.005}{1} = .005 M$.

$$H_2SO_4 + 2H_2O \rightleftharpoons 2H_3O^+ + SO_4^{--}$$

one mole of H_2SO_4 give 2 moles of H_3O^+ ions.

$$H_3O^+ = 2 \times (H_2SO_4) = 2 \times 0.005 = 0.01 M$$

$$[H^+] = 10^{-2} M\ ;\ pH = 2$$

107. (c) CH_3COONH_4 is a simple buffer and called salt of weak acid.

108. (c) N.eq. for $HCl = \frac{0.4}{1000} \times 50 = 0.02$

N.eq. for $NaOH = \frac{0.2}{1000} \times 50 = 0.1$

Now $[OH^-]$ left $= 0.1 - 0.02$

$$[OH^-] = .08 = 8 \times 10^{-2} M$$

$$pOH = -\log 8 \times 10^{-2} M\ ;\ pOH = 1.0$$

109. (d) Buffer is mixture of weak base and its acid salt.

110. (b) $[NaOH] = 0.4/40\ mole/l. = 0.1 M$

$$[OH^-] = 10^{-1} M,\ [H^+] = 10^{-13} M,\ pH = 13$$

111. (d) $pH + pOH = 14,\ pH = 4,\ H^+ = 10^{-4}$ *mole/litre.*

112. (d) Buffer solution have constant *pH*. When we add the water into this buffer solution. So no effect on it.

113. (b) $Ba(OH)_2 \rightleftharpoons Ba^{2+} + 2OH^-$

One molecule on dissociation furnishes $2OH^-$ ions.

So, $[OH^-] = 2 \times 10^{-4} N$

$$N = M \times 2\ ;\ M = \frac{N}{2} = \frac{2 \times 10^{-4}}{2} = 10^{-4}$$

$$pOH = -\log[OH^-] = -\log(1 \times 10^{-4}) = -4$$

$$pH + pOH = 14;\ pH = 14 - 4 = 10.$$

114. (a) M.eq. of 0.10 $M\ HCl = \frac{0.10}{1000} \times 40 = 0.004 M$

M.eq. of 0.45 $M\ NaOH = \frac{0.45 \times 10}{1000} = 0.0045 M$

Now left $[OH^-] = 0.0045 - 0.004 = 5 \times 10^{-4}$ M

Total volume = 50 *ml*.

$$[OH^-] = \frac{5 \times 10^{-4}}{50} \times 1000;\ [OH^-] = 1 \times 10^{-2}$$

pOH = 2 ; *pH* = 14 – *pOH* = 12.

115. (c) 0.001 *M HCl* $= 10^{-3}\ M\ [H^+],\ pH = 3$.

116. (d)

$$[NaOH] = \frac{0.4}{40} = 0.01M;\quad [OH^-] = 10^{-2} M$$

$$[H^+] = 10^{-12},\ pH = -\log[H^+] = 12$$

117. (b) Those substance which give a proton is called Bronsted acid while CH_3COO^- doesn't have proton so it is not a Bronsted acid.

120. (c) $pH = -\log[H^+]$

121. (d) $pH + pOH = 14, pH = 4.0$

$pOH = 14 - pH$; $pOH = 14 - 4.0 = 10.0$

122. (b) $pH = 0$ means $[H^+] = 10^0 = 1M$. Hence solution is strongly acidic.

123. (c) As the solution is acidic, *pH* < 7. This is because $[H^+]$ from H_2O $(10^{-7} M)$ cannot be neglected in comparison to 10^{-10} *M HCl*.

124. (d) $H_3O^+ \rightleftharpoons OH^- + H_2$

$pOH + pH = 14$; $7 + 7 = 14$; $[H^+] + [OH^-] = 10^{-14}$

$10^{-7} + 10^{-7} = 10^{-14}$; $[OH^-] = 10^{-7}$ *gm ion/l.*

126. (b) When $pH = 2$**,** $[H^+] = 10^{-2} M$

127. (a) $[OH^-]$ ion conc. $= 0.05 \frac{mol}{l} = 5 \times 10^{-2} \frac{mol}{l}$

$pOH = -\log[OH^-] = -\log[5 \times 10^{-2}]$

$pOH = 1.30$**;** $pH + pOH = 14$

$pH = 14 - pOH = 14 - 1.30 = 12.7$

128. (c) When $pH = 3$, then $[H^+] = 10^{-3} M$

after that we increased the *pH* from 3 to 6 then $[H^+] = 10^{-6} M$ means reduced 1000 times.

129. (b) CO_2 is acidic oxide which on dissolution in water develops acidic nature.

130. (d) If *pH* of any solution is 2.

Then $[H^+] = 10^{-2} M$

If *pH* of any solution is just double then $pH = 4$ and $[H^+]$ will be 10^{-4}.

131. (c) A strong acid is not used to make a buffer.

132. (d) $pH = 1$ means $[H^+] = 10^{-1} M$

Hence $[H_2SO_4] = \frac{10^{-1}}{2} = \frac{1}{20} = 0.05M$

133. (c) The *pH* of blood is 7.4 due to presence of bicarbonates ions

134. (c) As the solution is acidic, *pH* < 7. This is because $[H^+]$ from H_2O $[10^{-7}]$ cannot be neglected in comparison to 10^{-8}

135. (a) *pH* will decrease because $[OH^-]$ increased due to this pOH is decreased.

136. (c) $[H^+] = 6 \times 10^{-4} M$

$pH = -\log[H^+] = -\log[6 \times 10^{-4}] = 3.22.$

137. (c) $0.01M\ HCl = 10^{-2}\ M\ [H^+],\ pH = 2$.

138. (c) Because buffer solution have a constant *pH*.

139. (c) $10^{-6}\ M\ HCl = 10^{-8} M [H^+]$. Also from H_2O

$[H^+] = 10^{-7} M$

Total $[H^+] = 10^{-7} + 10^{-8} = 10^{-7}[1 + 0.1] = 10^{-7}[1.1]$

Hence $pH = 7 - 0.0414 = 6.96$.

140. (b) $10^{-10} M\ \ HCl = 10^{-10}\ M\ [H^+]$. But *pH* $\neq 10$ because solution is acidic. This is because H^+ from $H_2O(10^{-7} M)$ cannot be neglected.

Total $[H^+] = 10^{-7} + 10^{-10}$

$= 10^{-7} + (1 + 10^{-3}) = 10^{-7}(1.001)$

That is why $pH = 7$ (slightly less than 7)

141. (b) $[H^+] = 1.00 \times 10^{-6}$ *mole/litre*

$pH = -\log[1.00 \times 10^{-6}]$; *pH* = 6.

142. (a) $[H^+]$ is in moles per litre.

143. (d) As the solution is acidic, $pH < 7$. This is because $[H^+]$ from H_2O $(10^{-7} M)$ cannot be neglected in comparison to 10^{-8}.

145. (b) *pH* of 0.001 *M HCl* $= 10^{-3} M[H^+]$, *pH* = 3.

146. (d) Because it can furnish H^+ ions in solutions.

147. (c) Because it is a strong acid.

$H^+ = 10^{-1}$

$pH = -\log[H^+] = -\log[10^{-1}]$; $pH = 1$.

148. (b) Buffer solution is a combination of weak acid and conjugate base. *NaCl* is a salt and *NaOH* is the base.

149. (a) $[H^+] = \sqrt{Kc} = \sqrt{10^{-5}\times 0.1} = 10^{-3}$, $pH = 3$.

150. (d) In $\frac{N}{10}$ *NaOH* have $[OH^-] = 10^{-1}M$ means $pOH = 1$ and then $pH + pOH = 14$

$pH = 14 - pOH = 13$.

151. (b) Borate ions are hydrolyzed to develop alkaline nature in solution.

152. (d) Less the *pH*, more acidic is the solution.

154. (b) The equal conc. of salt and acid.

155. (c) $pH = -\log K_a + \log\frac{[KCN]}{[HCN]}$

$$pH = -\log[5\times 10^{-10}] + \log\left(\frac{0.15}{1.5}\right) = 8.302$$

157. (c) $pH = pK_a + \log\frac{[\text{Salt}]}{[\text{Acid}]}$ equimolar means

$\frac{[\text{Salt}]}{[\text{Acid}]} = 1$;

$pH = 4.74 + 0 = 4.74$

158. (a) Because of *NaCl* is a salt of strong acid and strong base. So that it is neutral.

159. (c) When strong acid and strong base are react neutral salt are formed. So that *NaCl* is a neutral salt.

162. (d) $pH = -\log K_b + \log\frac{[\text{Salt}]}{[\text{Acid}]}$

$$pH = -\log[1.8\times 10^{-5}] + \log\frac{[\text{Salt}]}{1.0}$$

$$9 = 4.7 + \log\frac{[\text{Salt}]}{1.0};$$

$$\log\frac{[\text{Salt}]}{1.0} = 4.7 - 9 = -4.3$$

$$\frac{[\text{Salt}]}{1.0} = \text{Antilog}\frac{1}{4.3}; [\text{Salt}] = 1.8$$

163. (b) $pH = -\log K_b + \log\frac{[\text{salt}]}{[\text{acid}]}$

$$5 = -\log 10^{-4} + \log\frac{[\text{salt}]}{[\text{acid}]}$$

$$\log\frac{[\text{salt}]}{[\text{acid}]} = 1$$

$$\frac{[\text{salt}]}{[\text{acid}]} = \text{antilog}\,1 = 10:1$$

164. (a) 1 *M KOH* show highest *pH* value because it is a strong base.

165. (d) NH_4OH is a weak acid and NH_4Cl is a strong base salt.

166. (a) $pH = 13.6$

$pOH = 14 - 13.6 = 0.4$

$[OH^-] = \text{Antilog}(-0.4) = 0.3979$. So the value of $[OH^-]$ between $0.1\ M$ and $1\ M$

167. (d) Aspirin is a weak acid. Due to common ion effect it is unionised in acid medium but completely ionised in alkaline medium.

168. (b) $[H^+][OH^-] = 10^{-14}$; $(10^{-7})(10^{-7}) = 10^{-14}$

169. (c) $HCl = 10^0 M$ has $pH = 0$. The value of *pH* decreases as concentration further increases.

170. (a) Because pure water has a 7 *pH*.

171. (c) When concentration of $[H^+]$ increased then the value of *pH* is decreases.

$$pH = \log\frac{1}{[H^+]}$$

172. (c) The concentration of $[H^+] = 10^{-2}$ mole/litre

$pH = -\log[H^+] = -\log[10^{-2}]$; $pH = 2$

173. (d) Due to common ion effect.

174. (b) In water solution.

$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$

concentration of OH^- is increased so that solution become more basic and the *pH* is increased.

175. (a) Na_2CO_3 is basic in nature. So its *pH* is greater than 7.

176. (c) It is not a mixture of weak acid or base and their strong salt.

177. (a) $[H^+] = \text{Antilog}(-4.58)$;

$[H^+] = 2.63\times 10^{-5}$ moles/litre

178. (c) $10^{-2}\ M\ NaOH$ will give $[OH^-] = 10^{-2}$

$\therefore pOH = 2$, Also $pH + pOH = 14$

$\therefore pH = 12$.

179. (a) $pH = pK_a + \log\frac{[\text{Salt}]}{[\text{Acid}]}$

$$= -\log 2\times 10^{-5} + \log\frac{10\times 1}{50\times 2} = 4.$$

180. (b) 0.001 *M* $NaOH$ means $[OH^-] = 10^{-3}$; $pOH = 3$

$pH + pOH = 14$; $pH = 14 - 3$

$pH = 11$; $[H^+] = 10^{-11}$ mole-litre^{-1}

181. (c) $[H^+] = C.\alpha$

$$[H^+] = 0.1 \times \frac{1}{100} = 10^{-3}$$

$$pH = -\log[H^+] = -\log 10^{-3} = 3$$

182. (b) $pH = 4$

$$pH + pOH = 14\ ;\ pOH = 14 - pH$$

$$pOH = 14 - 4 = 10;\ [OH^-] = 10^{-10}M$$

183. (b) $pH = \log\frac{1}{[H^+]} = \log\frac{1}{[3 \times 10^{-3}]} = 2.523$

185. (c) It is a strong base.

186. (b) $[H^+]$Concentration in 0.01M HCl is $10^{-2}M$ because 0.01 M HCl have only H^+

$$HCl \rightleftharpoons H^+ + Cl^-.$$

187. (b) The value of H_3O^+ ions will not changed.

$$CH_3COOH + H_2O \rightleftharpoons CH_3COO^- + H_3O^+.$$

188. (a) H_2O_2 (Hydrogen peroxide) is a corrosive volatile liquid. It is slightly acidic in nature. Its pKa value is approximately 10^{-12}.

192. (b) $pH = \log\frac{1}{H^+}$; $pH = \log\frac{1}{10^{-3}}$; $pH = 3$.

193. (b) NH_3 is Lewis base because of one lone pair of electron.

194. (b) $\underset{}{Ba(OH)_2} \rightarrow \underset{.05M}{Ba^{+2}} + \underset{2\times 0.5M}{2OH^-}$

$$pOH = \log\frac{1}{[OH]^-} = \log\frac{1}{.1} = 1$$

$pH + pOH = 14$; $pH + 1 = 14$; $pH = 14 - 1 = 13$

195. (a) If concentration of acid is increases ten times in a buffer then pH of the solution is increase by one.

198. (b) $pH > 7 =$ Basic

It means contain more hydroxide ions than carbonate ions.

199. (a) At 7pH the concentration of OH^- and H^+ are equal.

200. (a,d) M.eq. of 0.01 $M\ HCl = \frac{.01 \times 100}{1000} = 1 \times 10^{-3}$

$$pH = 3$$

M.eq. of .02 $M\ H_2SO_4 = \frac{.04 \times 50}{1000} = 2 \times 10^{-3}$

M.eq. of .02 $M\ NaOH = \frac{0.02 \times 50}{1000} = 1 \times 10^{-3}$

Left $[H^+] = 2 \times 10^{-3} - 1 \times 10^{-3} = 1 \times 10^{-3}$; $pH = 3$

202. (a,b,c) Because buffer solution are mixture of weak acid or weak base and their salt.

203. (c) Because $pH = 8$ is basic nature but HCl is a strong acid.

204. (c) $H_2SO_4 = 0.05 \times 2$

$\therefore [H^+] = 0.1$ and $pH = 1$

205. (b) $Mg(OH)_2 \rightleftharpoons Mg^{2+} + 2OH^-$

$$K_{sp} = [Mg^{2+}][OH^-]^2$$

$$1 \times 10^{-12} = 0.01[OH^-]^2$$

$$[OH^-]^2 = 1 \times 10^{-10} \Rightarrow [OH^-] = 10^{-5}$$

$$[H^+] = 10^{-14}/10^{-5} = 10^9$$

$$pH = -\log[H^+] = -\log[10^{-9}] = 9$$

206. (b) $[OH^-] = 1 \times 10^{-5}$

$$pOH = -\log[OH^-] = 5$$

$$pH + pOH = 14 \Rightarrow pH = 14 - 5 = 9.$$

Critical Thinking Questions

1. (b) K_{sp} of $AgI = 1.5 \times 10^{-16}$

$10^{-8}\ M\ Ag^+$ and $10^{-8}\ M\ I^-$

Ionic product $= 10^{-16}$

$K_{sp} =$ Ionic produc

2. (a) $HClO$ is the weakest acid. Its conjugate base ClO^- is the strongest base.

3. (b) $B(OH)_3$ not have H^+

4. (a) $h = \frac{k_w}{k_a} = \frac{1 \times 10^{-14}}{4.5 \times 10^{-10}} = 2.22 \times 10^{-5}$

5. (d) $MX_4 \rightarrow \underset{s}{M} + \underset{4s}{4X}$; $K_{sp} = (4s)^4 s$; $K_{sp} = 256s^5$

$$s = \left(\frac{K_{sp}}{256}\right)^{1/5}.$$

6. (a) Lewis acid are electrophiles because they accept election pairs.

7. (c) Initial $\underset{2}{2HI} \rightleftharpoons \underset{0}{H_2} + \underset{0}{I_2}$

At equilibrium $2 - \alpha$ $\quad \frac{\alpha}{2} \quad \frac{\alpha}{2}$

$$= 2 - \alpha + \frac{\alpha}{2} + \frac{\alpha}{2} = 2.$$

8. (a) Because they have vacant *d*-orbital in central atom.

9. (a) Energy has to be spent for the total dissociation of weak acid.

10. (a) pK_a of acid $A = 4$; pK_a of acid $B = 5$

We know that $pK_a = -\log K_a$

∴ Acid *A* $K_a = 10^{-4}$

Acid *B* $K_a = 10^{-5}$

Hence *A* is ten times stronger than that of *B.*

11. (b) $\frac{\alpha_1}{\alpha_2} = \sqrt{\frac{K_{a_1}}{K_{a_2}}} = \sqrt{\frac{3.14\times10^{-4}}{1.6\times10^{-5}}} = 4:1$

12. (d) It is a salt of weak acid and weak base.

13. (c) $HA \rightleftharpoons H^+ + A^-$; $K_a = \frac{[H^+][A^-]}{[HA]}$ ......(i)

neutralization of the weak acid with strong base is

$HA + OH^- \rightleftharpoons A^- + H_2O$

$K = \frac{[A^-]}{[HA][OH^-]}$ ......(ii)

dividing (i) by (ii) $\frac{K_a}{K} = [H^+][OH^-]$

$= K_w = 10^{-14}$

$K = \frac{K_a}{K_w} = \frac{10^{-5}}{10^{-14}} = 10^9$.

14. (d) NH_4Cl undergoes cationic hydrolysis hence *pH* is >7 because the solution due to cationic hydrolysis in acids.

NaCN undergoes anionic hydrolysis hence *pH* is >7.

HCl is strong acid and *NaCl* is neutral solution.

Hence the *pH* of given solutions will increases.

$HCl < NaCl < NaCN < NH_4Cl$

15. (c) It is a $HClO_4$

16. (d) Smaller the $_pK_a$ value, strong the acid.

17. (d) It involves gain and loss of electron pair (Lewis concept).

18. (b) $H^-_{(aq.)} + H_2O_{(l)} \rightarrow OH^- + H_2$.

19. (b) $K_H = \frac{K_a}{K_w} = \frac{10^{-4}}{10^{-14}} = \frac{1}{10^{-10}} = 10^{10}$.

20. (d) Acidity is directly propotional to oxidation number. As the O.No. of *S, P* and *Cl* in H_2SO_3, H_3PO_3 & $HClO_3$ is +4, +3 & +5 respectively so decreasing order of acidity will be III > I > II.

21. (a) A substance which can donate a proton is known as acid so NH_4^+ will be a acid.

22. (b) Acetic acid is a weak acid.

23. (a) Because it is a acidic oxide.

24. (b) $[Ca^{2+}][F^-]^2 = \left[\frac{10^{-2}\times V}{2V}\right]\times\left[\frac{10^{-3}\times V}{2V}\right]^2$

$= 1.25\times10^{-9}$.

25. (a) The degree of hydrolysis of a salt of weak acid and weak base is independent of concentration of salt.

26. (c) $C = 0.1M$; $\alpha = 1\%$; $(H^+) = C\times\alpha$

$= 0.1\times\frac{1}{100} = 10^{-3}$; $(H^+) = 10^{-3}$; *pH* = 3.

27. (d) $HClO_4$ is a strong acid, because its oxidation no is + 7.

28. (d) Acceptor of electron pair is known as lewis acid. *S*, : $CH_2, (CH_3)_3B$ all can accept an electron pair so answer is (d).

29. (b) $Mg(OH)^2 \rightleftharpoons \underset{(s)}{Mg^{2+}} + \underset{(2s)^2}{2OH^-}$

$K_{sp} = 4S^3 \Rightarrow S = \sqrt[3]{\frac{K_{sp}}{4}} = \sqrt[3]{\frac{1.2\times10^{-11}}{4}}$

$S = 8.16\times10^{-4}$

30. (d) $K_a = \frac{[H^+][CN^-]}{[HCN^-]}$

$6.2\times10^{-10} = \frac{[H^+][0.02]}{[0.01]}$

$[H^+] = \frac{6.2\times10^{-10}\times0.01}{0.02} = 3.1\times10^{-10}$

31. (b) $\ddot{N}H_3$ presence of lone pair of electrons.

32. (a) $\underset{K_{sp}}{CuBr} \rightleftharpoons \underset{(S)}{Cu^+} + \underset{(S)}{Br^-}$

$K_{sp} = S^2 = (2\times10^{-4})^2 = 4\times10^{-8}\frac{mol^2}{l^2}$

33. (c) $\underset{(0.004\ x)}{Na_2SO_4} \rightleftharpoons \underset{2x}{2Na^+} + \underset{x}{SO_4^{2-}}$

Since both the solution are isotonic $0.004 + 2x = 0.01$

∴ $x = 3\times10^{-3}$

∴ Percent dissociation $= \frac{3\times10^{-3}}{0.004}\times100 = 75\%$.

34. (a) $Cr(OH)_3 \rightarrow \underset{x}{Cr^{+3}} + \underset{3x}{3OH^-}$

$K_{sp} = x.(3x)^3 = 27x^4$

$x = \sqrt[4]{\frac{K_{sp}}{27}}$; $x = \sqrt[4]{\frac{2.7 \times 10^{-31}}{27}}$

$x = 1 \times 10^{-8}$ *mole/litre.*

35. (a) $H^+ = c.\alpha = \sqrt{K_a.c}$

$pH = -\log\left(\sqrt{K_a.c}\right)^{1/2}$

$= \frac{1}{2}[-\log K_a - \log c]$

$= \frac{1}{2}[4.74 - \log 10^{-2}] = \frac{1}{2}[4.74 + 2] = 3.37$.

36. (b) $Ag_2SO_4 \rightleftharpoons \underset{4S^2}{2Ag^+} + \underset{S}{SO_4^{--}}$

$K_{sp} = 4S^3$; $K_{sp} = 2 \times 10^{-5}$

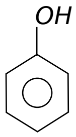
$S = \sqrt[3]{\frac{2 \times 10^{-5}}{4}} = 0.017 m/l = 1.7 \times 10^{-2}$

$Ag\,BrO_3 \rightleftharpoons \underset{S}{Ag^+} + \underset{S}{BrO_3^-}$

$K_{sp} = S^2$; $K_{sp} = 5.5 \times 10^{-5}$

$S = \sqrt{5.5 \times 10^{-5}} = 7.4 \times 10^{-3} m/l.$

37. (c)



Phenol are more acidic than ethanol because of stabilization of phenoxide as compare to ethoxide ion.

38. (b) $X^- + H_2O \rightleftharpoons HX + OH^-$

$K_h = \frac{10^{-14}}{10^{-5}}$ so $h = \sqrt{\frac{10^{-9}}{10^{-1}}} = 10^{-4}$

$100 \times 10^{-4} = 10^{-2}$

So, 0.01%.

39. (a) $K_a = 1.0 \times 10^{-5}$

K_h = hydrolysis constant

$K_h = \frac{K_w}{K_a} = \frac{10^{-14}}{10^{-5}} = 10^{-9}$

degree of hydrolysis (h) = $\sqrt{\frac{K_h}{C}}$

$= \sqrt{\frac{10^{-9}}{0.001}} = \sqrt{10^{-6}} = 10^{-3}$; $h = 10^{-3}$

40. (b) Basic radicals of group II & IV are precipitated by H_2S in the form of their sulphides. IInd group in acidic medium & IV group in alkaline medium. They precipitate when ionic product increases than solubility product.

41. (a) After mixing $[Ag^+][Cl^-] > K_{sp}$

42. (a) K_{sp} > ionic product $1 \times 10^{-10} > 5 \times 10^{-11}$

43. (a) 1 litre of water contains 1000/18 mole.

So degree of ionization $= \frac{10^{-7} \times 18}{1000} = 1.8 \times 10^{-7}$ %.

44. (a) *AgCl* $K_{sp} = 1.2 \times 10^{-10}$

$S = \sqrt{1.2 \times 10^{-10}}$; $S = 1.09 \times 10^{-5}$

AgBr $K_{sp} = 3.5 \times 10^{-13}$

$S = \sqrt{3.5 \times 10^{-13}} = 5.91 \times 10^{-6}$

So that *S* of *AgBr* is less than that of *AgCl*.

45. (a) $K_{sp} = 4S^3$

$4S^3 = 3.2 \times 10^{-8}$; $S = 2 \times 10^{-3} M$.

46. (c) $\frac{2.8 \times 10^{-10}}{0.1} = 2.8 \times 10^{-9} ML^{-1}$.

47. (b) $AB \rightleftharpoons A^+ + B^-$; $K_{sp} = S^2$

$S = \sqrt{K_{sp}} = \sqrt{4 \times 10^{-10}} = 2 \times 10^{-5}$

48. (b) $S = 1.435 \times 10^{-3}\, g/l$, $= \frac{1.435 \times 10^{-3}}{1435} = 10^{-5}$

M

$K_{sp} = S \times S = 10^{-10}$

49. (b) $pKa = 5$, so $Ka = 1 \times 10^{-5}$

$\alpha = \sqrt{\frac{Ka}{C}} = \sqrt{\frac{1 \times 10^{-5}}{0.1}} = 1 \times 10^{-2}$

50. (c) Presence of common ion decreases the solubility of salt.

51. (d) $Ag_2S > CuS > HgS$.

Solubility of *CuS* $= \sqrt{10^{-31}} = 3.16 \times 10^{-16}\, mol/lit$

Solubility of Ag_2S

$= \sqrt[3]{\frac{K_{sp}}{4}} = \sqrt[3]{\frac{10^{-42}}{4}} = 6.3 \times 10^{-5} mole/litre$

Solubility of *HgS* $= \sqrt{K_{sp}} = \sqrt{10^{-54}}$

$= 10^{-27}\, mol/litre$

52. (c) $pH = 3.82 = -\log[H^+]$

$\therefore [H^+] = 1.5 \times 10^{-4}$ *mole/litre.*

53. (b) $pH = pK_a + \log\frac{[\text{salt}]}{\text{acid}}$

$= 4.57 + \log\frac{0.10}{0.03} = 5.09$

54. (c) For a monobasic acid

$[H^+] = C\alpha$

$= \frac{1}{10} \times 0.001 = 10^{-4} \Rightarrow pH = 4$

55. (a) $K_{sp} = [As^{3+}][S^{2-}]$, $S = \sqrt[5]{\frac{K_{sp}}{108}}$

$= \sqrt[5]{\frac{2.8 \times 10^{-72}}{108}} = 1.09 \times 10^{-15}$

56. (d) Dissociation constant of $HA = 10^{-9}$

$HA \rightleftharpoons H^+ + A^-$

$[H^+] = \sqrt{\frac{K_a}{C}} = \sqrt{\frac{10^{-9}}{0.1}}$; $[H^+] = 10^{-4}$

$\therefore pH = 4$

$\because pH + pOH = 14$

$pOH = 14 - pH = 14 - 4$; $pOH = 10$

57. (d) $\alpha = 1.9 \times 10^{-9}$; $C = \frac{1000}{18}$

$K = \frac{[H^+][OH^-]}{(H_2O)} = C\alpha^2$

$= 1.9 \times 10^{-9} \times 1.9 \times 10^{-9} \times \frac{1000}{18}$

$= 2.0 \times 10^{-16}$.

58. (c) $K = Ka_1 \times Ka_2 = 4.5 \times 10^{-3} \times 1.7 \times 10^{10}$

$H^+ = \sqrt{Kc} = \sqrt{4.5 \times 10^{-3} \times 1.7 \times 10^{-10} \times .01}$

$= .87 \times 10^{-7}$

$pH = -\log 0.87 \times 10^{-7} = 7 - 0.93 = 6.07$.

59. (a) Given that

Concentration of solution $= .1$

Degree of ionisation $= 2\% = \frac{2}{100} = .02$

Ionic product of water $= 1 \times 10^{-14}$

Concentration of $[H^+]$= Concentration of solution X degree of ionisation $= .1 \times .02 = 2 \times 10^{-3} M$

Concentration of $[OH^-] = \frac{\text{Ionic prodct of water}}{[H^+]}$

$= \frac{1 \times 10^{-14}}{2 \times 10^{-3}} = 0.5 \times 10^{-11} = 5 \times 10^{-12} M$.

60. (a) $\underset{x}{HgSO_4 \rightarrow Hg^{++}} + \underset{x}{SO_4^{--}}$

$K_{sp} = x^2$; $x = \sqrt{K_{sp}}$; $x = \sqrt{6.4 \times 10^{-5}}$

$x = 8 \times 10^{-3}$ *mole/litre*.

61. (a) $K = c\alpha^2 = 0.1 \times \left(\frac{1.34}{100}\right)^2 = 1.8 \times 10^{-5}$.

62. (c)

$[H^+] = 1 \times 10^{-4} M \Rightarrow [H^+][OH^-] = 1 \times 10^{-14}$

$\therefore [OH^-] = \frac{1 \times 10^{-14}}{0.5 \times 10^{-4}} = 2 \times 10^{-10} M$

63. (d) Because $HClO_4$ is a strong acid. While buffer is a mixture of weak acid and their salt.

64. (b) Initial concentration = 0.006 M ⇒ $K_a = 6 \times 10^{-5}$

equilibrium reaction.

$$\underset{\substack{C\\C(1-a)}}{C_6H_5COOH} \rightleftharpoons \underset{\substack{O\\Ca}}{C_6H_5COO^-} + \underset{\substack{O\ \text{initial}\\Ca}}{H^+}$$

$K_a = C\alpha^2$ $(\because 1 - \alpha \approx 1)$ ***for weak electrolyte***

$\alpha = \sqrt{\frac{K_a}{C}}$ **;** $\alpha = \sqrt{\frac{6 \times 10^{-5}}{0.006}}$ **;** $\alpha = 10^{-1}$

$\because [H^+] = C\alpha = 0.006 \times 10^{-1} = 6 \times 10^{-4} M$.

65. (a) $pOH = pKb + \log\frac{[Salt]}{[Base]}$

$14 - 9.35 = -\log(1.78 \times 10^{-5}) + \log\frac{[Salt]}{100}$

$[Salt] = 79.9 \Rightarrow$ $\frac{w}{132} \times 1000 = 79.9 \Rightarrow$ $w = 10.56$

66. (a) $pH = 6$ means $[H^+] = 10^{-6} M$

$pH = 3$ means $[H^=] = 10^{-3} M$

After mixing,

Total $[H^+] = \frac{(10^{-6} + 10^{-3})}{2} = \frac{1.001 \times 10^{-3}}{2}$

$= 5.005 \times 10^{-4}$

$pH = 4 - \log 5.005$; $pH = 3.301$.

67. (b) $[H^+] = \sqrt{K \times C}$

$[H^+] = \sqrt{4 \times 10^{-10} \times 1}$; $[H^+] = 2 \times 10^{-5}$ *mole/litre*

68. (b) Moles of $[OH^-] = M \times V$

Number of $NaOH = 0.3 \times 0.005 \times 2 = 0.003$

69. (d) $[H^+][OH^-] = 10^{-13.26}$

$\therefore\ [H^+] = [OH^-]$, $\therefore\ [H^+]^2 = 10^{-13.26}$

$[H^+] = 10^{\frac{-13.26}{2}}$

pH = 6.63.

70. (b) $pH = pKa + \log\frac{[Salt]}{[Acid]}$

$pH = pKa$

$Ka = 0.1 \times (10^{-3.5})^2 = 0.1 \times 10^{-7} = 10^{-8}$ ⇒ $pH = 8$

71. (a) $pH = -\log K_a + \log\frac{[\text{Salt}]}{[\text{Acid}]}$

$[\text{Salt}] = \frac{0.2 \times 50}{1000} = 0.01$;

$[\text{Acid}] = \frac{0.5 \times 40}{1000} = 0.02$

$pH = -\log(1.8 \times 10^{-4}) + \log\frac{0.01}{0.02}$

$pH = 4 - \log(1.8) + \log 0.5$

$pH = 4 - \log(1.8) - 0.301$

$pH = 3.4$

72. (c) HCO_3^- and H_2O

73. (a) $[H^+] = C \times \alpha = 0.1 \times 0.1 = 10^{-2} M$

pH = 2; *pOH* = 12 ; $[OH^-] = 10^{-12} M$.

74. (c) Decreasing order of acidic character is $H_2SO_4 > CH_3COOH > H_2CO_3$

75. (c) The acidic nature increases in the order.

$NaNO_2 < NaCl < H_2S < H_2SO_4$

76. (a) $[OH^-] = 0.05 = 5 \times 10^{-2} M$

$pOH = 2 - \log 5 = 1.3$

$pH + pOH = 14$

$pH = 14 - 1.3 = 12.7$

77. (b) Na_2O form *NaOH*. So that it is basic oxide.

78. (a) $CH_3COO^- + H_2O \rightleftharpoons CH_3COOH + OH^-$

$\therefore [OH^-] = c \times h$; $h = \sqrt{\frac{K_w}{K_a} \times c}$

$= \sqrt{\frac{10^{-14}}{1.8 \times 10^{-5}} \times 1}$

$= 2.35 \times 10^{-5}$

$\therefore pOH = 4.62$; $pH = 9.38 \approx 9.4$

Assertion & Reason

1. (c) *HCl* is a strong electrolyte since it will produce more H^+, comparison than that of CH_3COOH. Hence assertion is true but reason false.

2. (b) For sparingly soluble salts, reason is not a correct explanation. Hence both assertion and reason are true but reason is not a correct explanation of assertion.

3. (a) Aq. solution of $FeCl_3$ on standing produce brown ppt. Due to hydrolysis it produce ppt. of $Fe(OH)_3$ which is of brown colour. Hence both are correct and reason is a correct explanation.

4. (a) Barium carbonate is more soluble in HNO_3 than in water become carbonate is a weak base and reacts with the H^+ ion of HNO_3 causing the barium salt to dissociate.

$BaCO_3 + HNO_3 \rightarrow Ba(NO_3)_2 + CO_2 + H_2O$

5. (a) The conjugate base of $CHCl_3$ is more stable than conjugate base of $CHF_3(CF_3)$. CCl_3 stabilized by –*I* effect of chlorine atoms as well as by the electrons. But conjugate base of $CH_3(CH_3)$ is stabilized only by –*I* effect of flourine atoms. Here both assertion and reason are true and reason is correct explanation of assertion.

6. (c) Ionic product of $AgBr$ is greater than that of $AgCl$ in comparison with there solubility product $AgBr$ will precipitate. First rather than that of $AgCl$.

9. (e) It is fact that ionic reactions are instantaneous due to the fact that oppositely charged ions exert strong forces and combine immediately.

EXERCISE # 1A

Q.1 Select the correct statement -

(1) If $[H^+] = y \times 10^{-x}$ then pH = x – log y

(2) If $[H^+] = \frac{1}{y} \times 10^{-x}$ then pH = x + log y

(3) pH of a solution = 14 + log $[OH^-]$

(4) All of the above

Q.2 Pure water ionises as

$2H_2O\,(\ell) \rightleftharpoons H_3O^+\,(aq.) + OH^-\,(aq)$

At 25º C the pH of pure water is approximately 7.0 At 37º C its pH is –

(1) More than 7.0 (2) Less than 7.0

(3) Equal to 7.0 (4) None of these

Q.3 For an acid solution the $[OH^-]$ is –

(1) $> 10^{-7}$ (2) $< 10^{-7}$ (3) 10^{-14} (4) 10^{-7}

Q.4 Select the correct combination –

(1) The aqueous solutions of each Na_3BO_3 and Na_3PO_4 – Acidic nature

(2) The aqueous solutions of each Na_3BO_3 and CH_3COONa – Basic nature

(3) The aqueous solutions of each CH_3COONa and NaCN – Acidic nature

(4) The aqueous solutions of each Na_3PO_4 and NH_4Cl – Acidic nature

Q.5 $pOH = 7 – 0.5\ pK_a + 0.5\ pK_b$ is true for which pair of cation and anion.

(1) $C_6H_5NH_3^+$, CH_3COO^-

(2) Na^+, CN^-

(3) Al^{+3}, Cl^-

(4) NH_4^+, NO_3^-

Q.6 Formula for degree of hydrolysis 'h';

$h = [\,10^{-7}\,(K_aK_b)^{-½}]$ is applicable to the salt –

(1) NH_4CN (2) $(NH_4)_2SO_4$

(3) NH_4Cl (4) NH_4NO_3

Q.7 The pH of a solution is 6.0. In this solution –

(1) $[H^+] = 100\,[OH^-]$ (2) $[H^+] = 10\,[OH^-]$

(3) $[H^+] = [OH^-]$ (4) $[H^+] = [OH^-]$

Q.8 K_{sp} of AgCl is $1 \times 10^{-10.}$ Its solubility in 0.1 M KNO_3 will be –

(1) 10^{-5} moles/litre

(2) > 10^{-5} moles/litre

(3) < 10^{-5} moles/litre

(4) None of these

Q.9 At 298 K, how many milligrams of silver bromide can be dissolved in 20 litres of water –

$[K_{sp\,(AgBr)} = 5.0 \times 10^{-13}]$

(Atomic wt. Ag = 108, Br = 80)

(1) 2.66 (2) 3.66

(3) 4.66 (4) None of these

Q.10 A_2B_3 electrolyte is completely dissociated in aqueous solution as: $A_2B_3 \rightarrow 2A^{+3} + 3B^{-2}$ Number of A^{3+} ions would be equal to -

(1) B^{2-} ions (2) 3/2 of B^{2-} ions

(3) 2/3 of B^{2-} ions (4) 1/2 of B^{2-} ions

Q.11 The formula weight of H_2SO_4 is 98. The weight of the acid in 400 mL of 0.1 M solution is -

(1) 2.45 g (2) 3.92 g

(3) 4.90 g (4) 9.8 g

Q.12 Normality of 2M sulphuric acid is -

(1) 2N (2) 4N (3) N/2 (4) N/4

Q.13 If pH = 3.31, then find out $[H^+]$ (Approxy)

(1) 3.39×10^{-4} (2) 5×10^{-4}

(3) 3.0×10^{-3} (4) None

Q.14 If $[OH^-] = 5.0 \times 10^{-5}$ M then pH will be -

(1) 5 – log 5 (2) 9 + log 5

(3) log 5 – 5 (4) log 5 – 9

Q.15 Basicity of H_3PO_3 and H_3PO_2 are respectively -

(1) 1 and 2 (2) 2 and 3

(3) 3 and 2 (4) 2 and 1

Q.16 Which of the following electrolysis (weak) would give aqueous solution having 3Cα anion concentration -

(1) A_3B (2) A_3B_2

(3) A_2B_6 (4) A_3B_4

Q.17 Find out pH of solution having 2×10^{-3} moles of OH^- ion's in 2 litre solution -

(1) pH = 3 (2) pH = 3 + log2

(3) pH = 3 – log2 (4) pH = 11

Q.18 The pH of a soft drink is 3.82. The hydrogen ion concentration will be -

(1) 1.96×10^{-2} mol L^{-1} (2) 1.6×10^{-4} mol L^{-1}

(3) 1.96×10^{-5} mol L^{-1} (4) None of them

Q.19 The amount of acetic acid present in 100 mL of 0.1 M solution is -

(1) 0.30 g (2) 3.0 g (3) 0.60 g (4) None

Q.20 The number of milli equivalents of acid in 100 mL of 0.5N HCl solution is -

(1) 50 (2) 100 (3) 25 (4) 200

Q.21 If the molar concentration of PbI_2 is 1.5×10^{-3} mol L^{-1}, the concentration of iodide ions in g ion L^{-1} is -

(1) 3.0×10^{-3} (2) 6.0×10^{-3}

(3) 0.3×10^{-3} (4) 0.6×10^{-6}

Q.22 Which one of the following has highest pH -

(1) Distilled water

(2) 1 M NH_3

(3) 1 M NaOH

(4) Water saturated with chlorine

Q.23 Order of dissociation of 0.1 N CH_3COOH is –

(Dissociation constant = 1×10^{-5})

(1) 10^{-5} (2) 10^{-4} (3) 10^{-3} (4) 10^{-2}

Q.24 If α is the degree of dissociation of weak dibasic organic acid and y is the hydrogen ion concentration, what is the initial concentration of acid -

(1) $\frac{\alpha(y)^{-1}}{2}$ (2) $y(\alpha)^{-1}$

(3) $\frac{y(\alpha)^{-1}}{2}$ (4) None of them

Q.25 The degree of dissociation of acetic acid is given by the expression $\alpha = 0.1 \times C^{-1}$ (where C = concentration of the acid) What is the pH of the solution -

(1) 1 (2) 2 (3) 3 (4) 4

Q.26 Ostwald's dilution law is not applicable for strong electrolytes because -

(1) Strong electrolytes are completely ionised

(2) Strong electrolytes are volatile

(3) Strong electrolytes are unstable

(4) Strong electrolytes often contain metal ions

Q.27 The degree of ionsation of a compound depends upon -

(1) Size of the solute molecules

(2) Nature of the solute molecules

(3) Nature of the container taken

(4) The amount of current passed

Q.28 Find out K_a for 10^{-2} M HCN acid, having pOH is 10 -

(1) $K_a = 10^{-4}$ (2) $K_a = 10^{-2}$

(3) $K_a = 10^{-5}$ (4) None of them

Q.29 The pH of 0.15 M solution of HOCl ($K_a = 9.6 \times 10^{-6}$) is -

(1) 4.42 (2) 2.92 (3) 3.42 (4) None

Q.30 The extent of ionization increases (weak electrolytes) -

(1) With the increase in concentration of solute

(2) On decreasing the temp. of solution

(3) On addition of excess of water to the solution

(4) On stirring the solution vigorously

Q.31 If Ka of HCN = 4×10^{-10}, then the pH of 2.5×10^{-1} molar HCN (aq) is -

(1) 4.2 (2) 4.7 (3) 0.47 (4) 5.0

Q.32 The molarity of nitrous acid at which its pH becomes 2. ($K_a = 4.5 \times 10^{-4}$) -

(1) 0.3333 (2) 0.4444

(3) 0.6666 (4) 0.2222

Q.33 Ionic product of water will increase. if -

(1) Decrease the pressure

(2) Add H^+

(3) Add OH^-

(4) Increase the temperature

Q.34 For water at 25° C, 2×10^{-7} moles per litre is the correct answer for which one of the following -

(1) $[H^+] + [OH^-]$ (2) $[H^+]^2$

(3) $[OH^-]^2$ (4) $[H^+] - [OH^-]$

Q.35 The pH of 1 N H_2O is -

(1) 7 (2) > 7 (3) < 7 (4) 0

Q.36 At 25°C, the dissociation constant for pure water is given by -

(1) $(55.4 \times 10^{14})^{-1}$ (2) 1×10^{-14}

(3) $\dfrac{1 \times 10^{-14}}{18}$ (4) None of these

Q.37 Ionic product of water is equal to -

(1) Dissociation constant of water × $[H_2O]$

(2) Dissociation constant of water × $[H^+]$

(3) Product of $[H_2O]$ and $[H^+]$

(4) Product of $[OH^-]^2$ and $[H^+]$

Q.38 Addition of H^+ and OH^- ion's concentration at 90°C -

(1) 10^{-14} (2) 10^{-12}

(3) 2×10^{-6} (4) 2×10^{-7}

Q.39 The units of ionic product of water (K_w) are -

(1) $mol^{-1}\ L^{-1}$(2) $mol^{2-}\ L^{-2}$

(3) $mol^{2-}\ L^{-1}$(4) $mol^{2}\ L^{-2}$

Q.40 At 373 K, temp. the pH of pure H_2O can be -

(1) < 7 (2) > 7 (3) = 7 (4) = 0

Q.41 Choose the correct relation -

(1) $\dfrac{pH + pOH}{14} = 7$ (2) pH + pOH = 14

(3) pOH = 14 + pH (4) pH = 14 + pOH

Q.42 Which of the following is a true statement -

(1) The ionisation constant and ionic product of water are same

(2) Water is a strong electrolyte

(3) The value of ionic product of water is less than that of its ionization constant

(4) At 298 K, the number of H^+ ions in a litre of water is 6.02×10^{16}

Q.43 Which of the following is not an acidic salt -

(1) $NaHSO_4$ (2) HCONa

(3) NaH_2PO_3 (4) None of them

Q.44 Which is a basic salt -

(1) PbS (2) $PbCO_3$

(3) $PbSO_4$ (4) $2PbCO_3\ Pb(OH)_2$

Q.45 The process of neutralization invariably results in the production of -

(1) H^+ ions

(2) OH^- ions

(3) Both H^+ and OH^- ions

(4) Molecules of water

Q.46 Which of the following is an acid salt -

(1) Na_2S (2) Na_2SO_3

(3) $NaHSO_3$ (4) Na_2SO_4

Q.47 At 90°C, the pH of 0.1 M NaCl aqueous solution is -

(1) < 7 (2) > 7 (3) 7 (4) 0.1

Q.48 What will the pH of 1.0 M ammonium formate solution. If $K_a = 1 \times 10^{-4}$ acid $K_b = 1 \times 10^{-5}$ -

(1) 6.5 (2) 7.5 (3) 8.0 (4) 9.0

Q.49 Which salt will not hydrolysis -

(1) KCl (2) Na_2SO_4

(3) NaCl (4) All

Q.50 The pH of aqueous solution of sodium acetate is -

(1) 7 (2) Very low

(3) > 7 (4) < 7

Q.51 pH of K_2S solution is -

(1) 7 (2) Less than 7

(3) More than 7 (4) 0

Q.52 For anionic hydrolysis, pH is given by -

(1) $pH = \frac{1}{2}pK_w - \frac{1}{2}pK_b - \frac{1}{2}\log c$

(2) $pH = \frac{1}{2}pK_w + \frac{1}{2}pK_a - \frac{1}{2}pK_b$

(3) $pH = \frac{1}{2}pK_w + \frac{1}{2}pK_a + \frac{1}{2}\log c$

(4) None of these

Q.53 Hydroxyl ion concentration $[OH^-]$ in the case of sodium acetate can be expressed as (where K_a is dissociation constant of CH_3COOH and C is the concentration of sodium acetate) -

(1) $[OH^-] = (CK_w \cdot K_a)^{1/2}$

(2) $[OH^-] = C.K_w\sqrt{K_a}$

(3) $[OH^-] = \left(\frac{C.K_w}{K_a}\right)^{1/2}$

(4) $[OH^-] = C.\ K_a \cdot K_w \cdot$

Q.54 Consider -

(1) $FeCl_3$ in water - Basic

(2) NH_4Cl in water - Acidic

(3) Ammonium acetate in water – Acidic

(4) Na_2CO_3 in water – Basic

which is/are not correctly match

(1) b & d (2) b only

(3) a & c (4) d only

Q.55 Which of the following salts undergoes hydrolysis in water -

(1) Na_3PO_4 (2) CH_3COONa

(3) $NaNO_3$ (4) Both of (1) and (2)

Q.56 A salt 'X' is dissolved in water of pH = 7. The resulting solution becomes alkaline in nature. The salt is made up of -

(1) A strong acid and strong base

(2) A strong acid and weak base

(3) A weak acid and weak base

(4) A weak acid and strong base

Q.57 Degree of Hydrolysis of $\frac{N}{100}$ solution of KCN is (Given Ka = 1.4×10^{-9})

(1) 2.7×10^{-3} (2) 2.7×10^{-2}

(3) 2.7×10^{-4} (4) 2.7×10^{-5}

Q.58 At 25°C, the K_{sp} value of AgCl is 1.8×10^{-10}. If 10^{-5} moles of Ag^+ are added to solution then K_{sp} will be -

(1) 1.8×10^{-15} (2) 1.8×10^{-10}

(3) 1.8×10^{-5} (4) $18 \times 10^{+10}$

Q.59 Concentration of Ag^+ ions in saturated solution of Ag_2CrO_4 at 20°C is 1.5×10^{-4} mol L^{-1}. At 20°C, the solubility product of Ag_2CrO_4 is -

(1) 3.3750×10^{-12} (2) 1.6875×10^{-10}

(3) 1.68×10^{-12} (4) 1.6875×10^{-11}

Q.60 If the concentration of CrO_4^{2-} ion in a saturated solution of silver chromate will be 2×10^{-4} M, solubility product of silver chromate will be -

(1) 4×10^{-8} (2) 8×10^{-12}

(3) 32×10^{-12} (4) 6×10^{-12}

Q.61 If the salts M_2X, QY_2 and PZ_3 have the same solubilities, their K_{sp} value are related as -(S < 1)

(1) $K_{sp}(M_2X) = K_{sp}(QY_2) < K_{sp}(PZ_3)$

(2) $K_{sp}(M_2X) > K_{sp}(QY_2) = K_{sp}(PZ_3)$

(3) $K_{sp}(M_2X) = K_{sp}(QY_2) > K_{sp}(PZ_3)$

(4) $K_{sp}(M_2X) > K_{sp}(QY_2) > K_{sp}(PZ_3)$

Q.62 The solubility product of As_2S_3 is given by the expression -

(1) $K_{sp} = [As^{3+}] \times [S^{-2}]$ (2) $K_{sp} = [As^{3+}]^1\ [S^{-2}]^1$

(3) $K_{sp} = [As^{3+}]\ [S^{-2}]^2$ (4) $K_{sp} = [As^{3+}]^2\ [S^{-2}]^3$

Q.63 If the solubility of $PbBr_2$ is 'S' g molecules per litre, considering 100% ionization it solubility product is -

(1) $2S^3$ (2) $4S^2$ (3) $4S^3$ (4) $2S^4$

Q.64 If the solubility of lithium sodium hexeafluoro aluminate $Li_3Na_3(AlF_6)_2$ is 'S' mol L^{-1}. Its solubility product is equal to -

(1) S^8 (2) $12\ S^3$ (3) $18S^3$ (4) $2916\ S^8$

Q.65 At 30°C, In which of the one litre solution, the solubility of Ag_2CO_3 (solubility product = 8×10^{-12}) will be maximum -

(1) 0.05 M Na_2CO_3 (2) Pure water

(3) 0.05 M $AgNO_3$ (4) 0.05 M NH_3

Q.66 Solubility of AgBr will be minimum in -

(1) Pure water (2) 0.1 M $CaBr_2$

(3) 0.1 M NaBr (4) 0.1 M $AgNO_3$

Q.67 In which of the following, the solution of AgSCN will be unsaturated -

(1) $[Ag^+]\ [SCN^-] = K_{sp}$ (2) $[Ag^+] \times [SCN^-] < K_{sp}$

(3) $[Ag^+] \times [SCN^-] > K_{sp}$ (4) $[Ag^+]\ [SCN^-]^2 < K_{sp}$

Q.68 If 's' and 'S' are respectively solubility and solubility product of a sparingly soluble binary electrolyte then -

(1) s = S (2) $s = S^2$

(3) $s = S^{1/2}$ (4) $s = \frac{1}{2}S$

Q.69 The solubility product of CuS, Ag_2S and HgS are 10^{-37}, 10^{-44} and 10^{-54} respectively. The solubility of these sulphides will be in the order -

(1) HgS > Ag_2S > CuS (2) Ag_2S > HgS > CuS

(3) CuS > Ag_2S > HgS (4) Ag_2S > CuS > HgS

Q.70 If the maximum concentration of $PbCl_2$ in water is 0.01 M at 298 K. Its maximum concentration in 0.1 M NaCl will be -

(1) 4×10^{-3} M (2) 0.4×10^{-4} M

(3) 4×10^{-2} M (4) 4×10^{-4} M

Q.71 Which of the following has maximum solubility (K_{sp} value is given in brackets) -

(1) HgS (1.6×10^{-54}) (2) $PbSO_4$ (1.3×10^{-8})

(3) ZnS (7.0×10^{-26}) (4) AgCl (1.7×10^{-10})

Q.72 Maximum soluble is - (K_{sp} is given)

(1) CuS (8.5×10^{-36}) (2) CdS (3.6×10^{-28})

(3) ZnS (1.2×10^{-28}) (4) MnS (1.4×10^{-10})

Q.73 In which of the following, the solubility of AgCl will be maximum -

(1) 0.1 M $AgNO_3$ (2) Water

(3) 0.1 M NaCl (4) 0.1 M KCl

Q.74 The solubility product of three sparingly soluble salts are given below -

No.	**Formula Product**	**Solubility**
i	PQ	4.0×10^{-20}
ii	PQ_2	3.2×10^{-14}
iii	PQ_3	2.7×10^{-35}

The correct order of decreasing molar solubility is -

(1) i,ii, iii (2) ii, i, iii

(3) iii, ii, i (4) ii, iii, i

Q.75 The K_{sp} value for $Gd(OH)_3$ is 2.8×10^{-23}, the pH at which $Gd(OH)_3$ begins to precipitate is -

(1) 6.08 (2) 5.08 (3) 8.47 (4) 4.08

Q.76 If the solubility product of $AgBrO_3$ and Ag_2SO_4 are 5.5×10^{-5} and 2×10^{-5} respectively, the relationship between the solubilities of these can be correctly represented as -

(1) $sAgBrO_3 > sAg_2SO_4$

(2) $sAgBrO_3 = sAg_2SO_4$

(3) $sAgBrO_3 < sAg_2SO_4$

(4) $sAgBrO_3 = sAgSO_4$

Q.77 0.5 M HCl solution has ions$^-$ Hg^{++}, Cd^{++}, Fe^{++}, Cu^{++}. To pass the H_2S gas in this solution, which are precipitated out -

(1) Cd^{+2}, Fe^{+2}, Sr^{+2} (2) Cd^{+2}, Hg^{+2}, Cu^{+2}

(3) Hg^{+2}, Cu^{+2}, Fe^{+2} (4) Cu^{+2}, Sr^{+2}, Fe^{+2}

Q.78 In the qualitative analysis of group III, $Fe(OH)_2$ is not precipitated because -

(1) The K_{sp} for $Fe(OH)_2$ is higher

(2) To precipitate $Fe(OH)_2$, only small $[OH^-]$ is needed

(3) $Fe(OH)_2$ is a weak electrolyte

(4) The oxidation state of Fe in Fe $(OH)_2$ is + 2

Q.79 A solution, containing 0.01 M Zn^{+2} and 0.01 M Cu^{2+} is saturated by passing H_2S gas. The S^{-2} concentration is 8.1×10^{-21} M, Ksp for ZnS and CuS are 3.0×10^{-22} and 8.0×10^{-36} respectively. Which of the following will occur in the solution -

(1) ZnS will precipitate

(2) CuS will precipitate

(3) Both ZnS and CuS will precipitate

(4) Both Zn^{2+} and Cu^{2+} will remain in the solution

Q.80 Consider (1) $Zn(OH)_2$ (2) $Cr(OH)_3$ (3) $Mg(OH)_2$ (4) $Al(OH)_3$ which hydroxide is precipitated by NH_4OH containing NH_4Cl -

(1) 1, 2 (2) 2, 4

(3) Only 4 (4) 1, 2, 3 and 4

Q.81 The solubility product constant Ksp of $Mg(OH)_2$ is 9.0×10^{-12}. If a solution is 0.010 M with respect to Mg^{2+} ion, what is the maximum hydroxide ion concentration which could be present without causing the precipitation of Mg $(OH)_2$ -

(1) 1.5×10^{-7} M (2) 3.0×10^{-7} M

(3) 1.5×10^{-5} M (4) 3.0×10^{-5} M

Q.82 When HCl gas is passed through a saturated solution of common salt, pure NaCl is precipitated because -

(1) The impurities dissolve in HCl

(2) HCl is slightly soluble in water

(3) The ionic product $[Na^+] \times [Cl^-]$ exceeds the solubility product of NaCl

(4) The solubility product of NaCl is lowered by Cl^- from aq. HCl

Q.83 Why only As^{3+} gets precipitated as As_2S_3 and not Zn^{2+} as ZnS when H_2S is passed through an acidic solution containing As^{3+} and Zn^{2+} -

(1) Enough As^{3+} are present in acidic medium

(2) Zinc salt does not ionise in acidic medium

(3) Solubility product of As_2S_3 is less than that of ZnS

(4) Solubility product changes in presence of an acid

Q.84 H_2S is passed through a solution of cation in HCl medium to precipitate cation of -

(1) II-A group of cation analysis

(2) II- B group of cation analysis
(3) IV group of cation analysis
(4) Both II- A and II-B gps.

Q.85 The solubility product of hydroxides of Mg^{+2}, Zn^{+2}, and Fe^{+3} decreases as
K_{sp} $Mg(OH)_2$ > K_{sp} $Zn(OH)_2$ > K_{sp} $Fe(OH)_3$ The decreasing order of precipitation of hydroxides is -
(1) $Fe(OH)_3$, $Zn(OH)_2$, $Mg(OH)_2$
(2) $Mg(OH)_2$, $Zn(OH)_2$, $Fe(OH)_3$
(3) $Zn(OH)_2$, $Fe(OH)_3$, $Mg(OH)_2$
(4) $Zn(OH)_2$, $Mg(OH)_2$, $Fe(OH)_3$

Q.86 Find out (OH^-) concentration in pH = 3.28 solution -
(1) 5.3×10^{-4} (2) 5.3×10^{-10}
(3) 1.8×10^{-10} (4) 1.8×10^{-11}

Q.87 What is H^+ ion concentration of 5×10^{-3} M H_2CO_3 solution having a 10% dissociation -
(1) 10^{-3} (2) 10^{-2}
(3) 10^{-1} (4) 5×10^{-2}

EXERCISE # 1B

Q.1 According to Lewis concept acid and base pair is -
(1) H^+ (2) Ag, Cl^-
(3) BF_3, NH_3 (4) None of these

Q.2 A 0.01 M acetic acid solution is 1.0% ionised. An another acetic acid is 10% ionised. What will be the concentration of another acetic acid –
(1) 0.001 M (2) 0.0001 M
(3) 0.01 M (4) 0.1 M

Q.3 For a 100 ml solution of 10^{-2} M NaOH the ratio pH: pOH would be –
(1) 6 : 1 (2) 1 : 6
(3) 2 :1 (4) 10^{10} : 1

Q.4 100 ml of 1.0 N CH_3COOH are added to 100 ml of 1.0 N NaOH solution. What will be the p^H of resulting solution –
(1) 7.0 (2) > 7.0 (3) < 7.0 (4) Zero

Q.5 According to Bronsted-Lowry concept, the relative strengths of the bases CH_3COO^-, OH^- and Cl^- are in the order -
(1) $OH^- > CH_3COO^- > Cl^-$
(2) $Cl^- > OH^- > CH_3COO^-$
(3) $CH_3COO^- > OH^- > Cl^-$
(4) $OH^- > Cl^- > CH_3COO^-$

Q.6 Which of the following acids is stronger than benzoic acid ($K_a = 6.3 \times 10^{-5}$) -
(1) A ($K_a = 1.62 \times 10^{-7}$)
(2) B ($pK_a = 6$)
(3) C ($pK_a = 4$)
(4) D ($K_a = 1.0 \times 10^{-5}$)

Q.7 Two monobasic weak acids have the same concentration of H^+ ions. What is the relationship between dissociation constant and dilution -
(1) $Ka_1 V_1 = Ka_2 V_2$ (2) $Ka_1V_2 = Ka_2V_1$
(3) $[Ka_1V_1]^{1/2} = Ka_2V_2$ (4) $Ka_1V_1 = [Ka_2V_2]^{1/2}$

Q.8 The pH of a 0.1 M formic acid 0.1% dissociated is equal to 4. What will be the pH of another weak acid (same concentration) which is 1% dissociated -
(1) 2 (2) 3 (3) 1 (4) 4

Q.9 pH of water is 7. When any substance Y is dissolved in water then pH becomes 13. Substance Y is a salt of -
(1) Strong acid and strong base
(2) Weak acid and weak base
(3) Strong acid and weak base
(4) Weak acid and strong base

Q.10 Minimum pH is shown by aqueous solution of -
(1) 0.1 M $BaCl_2$ (2) 0.1 M $Ba(NO_3)_2$
(3) 0.1 M $BeCl_2$ (4) 0.1 M $Ba(OH)_2$

Q.11 0.001 N KOH solution has the pH -
(1) 10^{-1} (2) 3 (3) 11 (4) 2

Q.12 Which of the following solution shows a pH = 7 -
(1) Aqueous solution of detergent
(2) Aqueous solution of potassium stearate
(3) Aqueous solution of hard soap
(4) Aqueous solution of soft soap

Q.13 Given : -

(1) 0.005 M H_2SO_4 (2) 0.1 M Na_2SO_4

(3) 10^{-2} M NaOH (4) 0.01 M HCl

Choose the correct code having same pH-

(1) a, c, d (2) b, d

(3) a, d (4) a, c

Q.14 A metal hydroxide of molecular formula $M(OH)_4$ is 50% ionized. Its 0.0025M solution will have the pH -

(1) 12 (2) 2 (3) 4 (4) 11.7

Q.15 In the following solutions, the conc. of different acids are given, which mixture of the acid has highest pH -

(1) $\frac{M}{10}$ H_2SO_4, $\frac{M}{20}$ HNO_3, $\frac{M}{10}$ $HClO_4$

(2) $\frac{M}{20}$ H_2SO_4, $\frac{M}{10}$ HNO_3, $\frac{M}{20}$ $HClO_4$

(3) $\frac{M}{20}$ H_2SO_4, $\frac{M}{10}$ HNO_3, $\frac{M}{40}$ $HClO_4$

(4) $\frac{M}{20}$ H_2SO_4, $\frac{M}{5}$ HNO_3, $\frac{M}{5}$ $HClO_4$

Q.16 If 100 mL of pH = 3 and 400 mL of pH = 3 is mixed, what will be the pH of the mixture -

(1) 3.2 (2) 3.0 (3) 3.5 (4) 2.8

Q.17 10^{-6} M HCl is diluted to 100 times. Its pH is

(1) 6.0 (2) 8.0 (3) 6.95 (4) 9.5

Q.18 pH of 0.001 M acetic acid would be -

(1) 2 (2) > 3 (3) 7 (4) 14

Q.19 At 90°C, the pH of 0.001 M KOH solution will be -

(1) 3 (2) 11 (3) 5 (4) 9

Q.20 An aqueous solution of Rochelle's salt is -

(1) Neutral (2) Acidic

(3) Basic (4) Does not hydrolyse

Q.21 The pH of a solution is defined by the equation -

(1) $pH = -\log [H_3O^+]$ (2) $pH = \log \frac{1}{[H_3O^+]}$

(3) $[H^+] = 10^{-pH}$ (4) All

Q.22 The pH of the solution containing 10 mL of a 0.1 M NaOH and 10 mL of 0.05M H_2SO_4 would be -

(1) Zero (2) 1 (3) >7 (4) 7

Q.23 In a solution of pH = 5, more acid is added in order to reduce the pH = 2. The increase in hydrogen on concentration is -

(1) 100 times (2) 1000 times

(3) 3 times (4) 5 times

Q.24 The hydrogen ion concentration in a given solution is 6×10^{-4} M. Its pH will be -

(1) 6 (2) 3.22 (3) 4 (4) 2

Q.25 The pOH of beer is 10.0. The hydrogen ion concentration will be -

(1) 10^{-10} (2) $\frac{K_W}{10^{-10}}$ (3) $\frac{K_W}{10^{-8}}$

(4) 10^{-4}

(1) a, d (2) b, c

(3) a, b, c (4) None

Q.26 An aqueous solution whose pH = 0 is -

(1) Basic (2) Acidic

(3) Neutral (4) Amphoteric

Q.27 The pH of a 10^{-10} M NaOH solution is nearest to -

(1) 10 (2) 7 (3) 4 (4) – 10

Q.28 The pH of a 0.02 M ammonia solution which is 5% ionized will be -

(1) 2 (2) 11 (3) 5 (4) 7

Q.29 Pure water is kept in a vessel and it remains exposed to atmospheric CO_2 which is absorbed. Then the pH will be -

(1) Greater than 7

(2) Less than 7

(3) 7

(4) Depends on ionic product of water

Q.30 For $\frac{N}{10}$ H_2SO_4 , pH value is -

(1) 1 (2) 0.586

(3) 0.856 (4) None

Q.31 An aqueous solution of HCl is 10^{-9} M HCl. The pH of the solution should be -

(1) 9 (2) Between 6 and 7

(3) 7 (4) Unpredictable

Q.32 H_2X is a dibasic acid which dissociated completely in water. Which one of the following is the molarity of an aqueous solution of this acid which has a pH of 1 -

(1) 0.1 (2) 0.05 (3) 0.2 (4) 0.5

Q.33 The pH of blood is -

(1) Less than 6

(2) Greater than 7 and less than 8

(3) Greater than 8 and less than 9

(4) Greater than 10

Q.34 The pH of gastric juice is normally -

(1) Less than 1.2

(2) Less than 0

(3) Greater than 1 and less than 3

(4) Less than 1 and greater than zero

Q.35 8 g NaOH and 4.9 g H_2SO_4 are present in one litre of the solution. What is the its pH

(1) 1 (2) 13 (3) 12 (4) 2

Q.36 Calculate pH of solution whose 100 mL contains 0.2 g NaOH dissolved in it -

(1) 10.699 (2) 11.699

(3) 12.699 (4) 13.699

Q.37 What is the quantity of NaOH present in 250 cc of the solution, so that it gives a pH = 13 -

(1) 10^{-13} g (2) 10^{-1} g

(3) 1.0 g (4) 4.0 g

Q.38 0.001 mol of the strong electrolyte $M(OH)_2$ has been dissolved to make a 20 mL of its saturated solution. Its pH will be – $[K_w = 1 \times 10^{-14}]$

(1) 13 (2) 3.3 (3) 11 (4) 9.8

Q.39 Choose the wrong statement -

(1) For a neutral solution : $[H^+] = [OH^-] = \sqrt{K_w}$

(2) For an acidic solution : $[H^+] > \sqrt{K_w}$ and $[OH^-] < \sqrt{K_w}$

(3) For a basic solution : $[H^+] < \sqrt{K_w}$ and $[OH^-] > \sqrt{K_w}$

(4) For a neutral solution at all temperatures $[H^+] = [OH^-] = 10^{-7}$ M

Q.40 A solution of H_3BO_3 and borax is called -

(1) Acidic buffer (2) Basic buffer

(3) Basic solution (4) None of these

Q.41 In a buffer solution the ratio of concentration of NH_4Cl and NH_4OH is 1 : 1 when it changes in 2 : 1 what will be the value of pH of buffer -

(1) Increase (2) Decrease

(3) No effect (4) N.O.T.

Q.42 In the volumetric estimation of HCl, if we make use of phenolphthalein as an indicator, which base is unsuitable for the titration -

(1) NaOH (2) RbOH

(3) KOH (4) NH_4OH

Q.43 In a mixture of weak acid and its salt, the ratio of concentration of acid to salt is increased ten fold. The pH of the solution -

(1) Decrease by one (2) Increases by one-tenth

(3) Increase by one (4) Increase ten-fold

Q.44 pK_b for NH_4OH at certain temperature is 4.74. The pH of basic buffer containing equimolar concentration of NH_4OH and NH_4Cl will be -

(1) 7.74 (2) 4.74 (3) 2.37 (4) 9.26

Q.45 What is the suitable indicator for titration of NaOH and oxalic acid -

(1) Methyl orange (2) Methyl red

(3) Phenolphthalein (4) Starch solution

Q.46 Phenolphthalein does not act as an indicator for the titration between -

(1) KOH and H_2SO_4

(2) NaOH and CH_3COOH

(3) Oxalic acid and $KMnO_4$

(4) $Ba(OH)_2$ and HCl

Q.47 The buffer solution play an important role in -

(1) Increasing the pH value

(2) Decreasing the pH value

(3) Keeping the pH constant

(4) Solution will be neutral

Q.48 Ka for HCN is 5×10^{-10} at 25°C. For maintaining a constant pH of 9, the volume of 5M KCN solution required to be added to 10mL of 2M HCN solution is -

(1) 4 mL (2) 7.95 mL
(3) 2 mL (4) 9.3 mL

Q.49 Buffering action of a mixture of CH_3COOH and CH_3COONa is maximum when the ratio of salt to acid is equal to -

(1) 1.0 (2) 100.0 (3) 10.0 (4) 0.1

Q.50 The pink colour of phenolphthalein in alkaline medium is due to -

(1) Negative ion (2) Positive ion
(3) OH^- ions (4) Neutral form

Q.51 Which indicator works in the pH range 8 – 9.8 -

(1) Phenolphthalein (2) Methyl orange
(3) Methyl red (4) Litmus

Q.52 A basic – buffer will obey the equation $pOH - pK_b = 1$ only under condition -

(1) [Conjugate acid] : [base] = 1 : 10
(2) [Conjugate acid] = [base]
(3) [Conjugate acid] : [base] = 10 : 1
(4) N.O.T

Q.53 For weak acid, strong base titration, the indicator used is -

(1) Potassium di- chromate
(2) Methyl orange
(3) Litmus
(4) Phenolphtalein

Q.54 From the following in which titration methyl orange is a best indicator -

(1) $CH_3COOH + NaOH$
(2) $H_2C_2O_4 + NaOH$
(3) $HCl + NaOH$
(4) $CH_3COOH + NH_4OH$

Q.55 The total number of different kind of buffers obtained during the titration of H_3PO_4 with NaOH are -

(1) 3 (2) 1 (3) 2 (4) 0

Q.56 A certain acidic buffer solution contains equal concentration of X^- and HX. The K_b for X^- is 10^{-10}. The pH of buffer is -

(1) 4 (2) 7 (3) 10 (4) 14

Q.57 When 1.0 mL of dil. HCl acid is added to 100 mL of buffer solution of pH 4.0. The pH of solution.

(1) Becomes 7 (2) Does not change
(3) Becomes 2 (4) Becomes 10

Q.58 The pH of blood is maintained by CO_2 and H_2CO_3 in the body and chemical constituents of blood. This phenomenon is called -

(1) Colloidal (2) Buffer action
(3) Acidity (4) Salt balance

Q.59 Phenolphthalein is not a good indicator for titrating -

(1) NaOH against oxalic acid
(2) NaOH against HCl
(3) NaOH against H_2SO_4
(4) Ferrous sulphate against $KMnO_4$

Q.60 Which of the following solutions does not act as buffer -

(1) $H_3PO_4 + NaH_2PO_4$
(2) $NaHCO_3 + H_2CO_3$
(3) $NH_4Cl + HCl$
(4) $CH_3COOH + CH_3COONa$

Q.61 50 mL of 2N acetic acid mixed with 10 mL of 1N sodium acetate solution will have an approximate pH of ($K_a = 10^{-5}$) -

(1) 4 (2) 5 (3) 6 (4) 7

Q.62 A solution contains 0.2M NH_4OH and 0.2M NH_4Cl. If 1.0 mL of 0.001 M HCl is added to it. What will be the $[OH]^-$ of the resulting solution [$K_b = 2 \times 10^{-5}$]

(1) 2×10^{-5} (2) 5×10^{-10}
(3) 2×10^{-3} (4) None of these

Q.63 Hunderson equation $pH - pK_a = 5$ will be applicable to an acidic buffer when -

(1) [Acid] = [Conjugate base]
(2) [Acid] × 10^5 = [Conjugate base]
(3) [Acid] = [Conjugate base] × 10^5
(4) None of these

Q.64 0.05 M ammonium hydroxide solution is dissolved in 0.001 M ammonium chloride solution. What will be the OH^- ion concentration of this solution $K_b(NH_4OH) = 1.8 \times 10^{-5}$

(1) 3.0×10^{-3} (2) 9.0×10^{-4}
(3) 9.0×10^{-3} (4) 4.0×10^{-4}

Q.65 When 0.02 moles of NaOH are added to a litre of buffer solution , its pH changes from 5.75 to 5.80. What is its buffer capacity -

(1) 0.4 (2) 0.05

(3) – 0.05 (4) 2.5

Q.66 Calculate the pH of a buffer prepared by mixing 300 cc of 0.3 M NH_3 and 500 cc of 0.5 M NH_4Cl. K_b of $NH_3 = 1.8 \times 10^{-5}$ -

(1) 8.1187 (2) 9.8117

(3) 8.8117 (4) None of these

Q.67 What amount of sodium propanoate should be added to one litre of an aqueous solution containing 0.02 mole propanoic acid (Ka = 1.34×10^{-5} at 25ºC) to obtain a buffer solution of pH 4.75 -

(1) 4.52×10^{-2} M (2) 3.52×10^{-2} M

(3) 2.52×10^{-2} M (4) 1.52×10^{-2} M

Q.68 When 20 mL of $\frac{M}{20}$ NaOH are added to 10 mL of $\frac{M}{10}$ HCl, the resulting solution will -

(1) Turn blue litmus red

(2) Turn phenolphthalein solution

(3) Turn methyl orange red

(4) Will have no effect on either red or blue litmus

Q.69 10 mL of a solution contains 0.1 M NH_4Cl + 0.01 M NH_4OH. Which addition would not change the pH solution -

(1) Adding 1 mL water

(2) Adding 5 mL of 0.1 M NH_4Cl

(3) Adding 5 mL of 0.1 M NH_4OH

(4) Adding 10 mL of 0.1 M NH_4Cl

Acid - Base

Q.70 Maximum lewis acid character is shown by which ion's -

(1) B^{+3} (2) Li^+

(3) Na^+ (4) Cs^+

Q.71 The conjugated acid of O^{-2} ion's is -

(1) O_2^+ (2) H^+ (3) H_3O^+ (4) OH^-

Q.72 Amphoteric oxide is -

(1) NO_2 (2) CO_2

(3) Al_2O_3 (4) (1) and (3) both

Q.73 Ionization constant of AOH and BOH base one K_{b_1} and K_{b_2}. Their relation is $pK_{b_1} < pK_{b_2}$. Conjugate of following base, does not show maximum pH -

(1) AOH (2) BOH

(3) Both of them (4) NOT

Q.74 If (a) OH^- (b) NH_2^- (c) H^-

The decreasing order of acidic strength of the above species will be -

(1) $OH^- > NH_2^- > H^-$ (2) $NH_2^- > OH^- > H^-$

(3) $H^- > NH_2^- > OH^-$ (4) $H^- > OH^- > NH_2^-$

Q.75 Anhydride of perchloric acid will be -

(1) Cl_2O (2) Cl_2O_7 (3) Cl_2O_3 (4) ClO_2

Q.76 Select the species which can function as - Lewis base, bronsted acid and bronsted base -

(1) H_2O (2) NH_4^+ (3) N^{-3}

Correct code is

(1) Only a (2) a, b

(3) a, c (4) b, c

Q.77 Which of the following oxy-acid is the strongest acid -

(1)H_3PO_4 (2) H_3AsO_4

(3) H_3SbO_4 (4) HNO_3

Q.78 Which ions does not show acid behaviour -

(1) $\left[Al(H_2O)_6\right]^{+3}$ (2) $\left[Fe(H_2O)_6\right]^{+3}$

(3) HPO_4^{-2} (4) ClO_3^-

Q.79 An example of Lewis acid is -

(1) CaO (2) CH_3NH_2

(3) SO_3 (4) None of these

Q.80 In the reaction $NH_3 + H_2O \rightleftharpoons NH_4^+ + OH$ water behaves as -

(1) Acid (2) Base

(3) Neutral (4) Both acid and Base

Q.81 Which acts as Lewis base in the reaction

$BCl_3 + :PH_3 \rightarrow Cl_3B \leftarrow PH_3$

(1) PH_3 (2) BCl_3

(3) Both 1 and 2 (4) None

Q.82 Which acts as Lewis acid in the reaction

$SnCl_2 + 2Cl^- \longrightarrow [SnCl_4]^{-2}$

(1) Cl^- (2) $SnCl_2$

(3) $SnCl_4$ (4) None

Q.83 The conjugated base of $(CH_3)_2\overset{+}{N}H_2$ is -

(1) CH_3NH_2 (2) $(CH_3)_2N^+$
(3) $(CH_3)_2N$ (4) $(CH_3)_2NH$

Q.84 Which is the strongest Lewis base -
(1) SbH_3 (2) AsH_3
(3) PH_3 (4) NH_3

Q.85 Weakest Lowry base is -
(1) H^- (2) OH^- (3) Cl^- (4) HCO_3^-

Q.86 Which equilibrium can be described as Lewis acid base reaction but not Bronsted acid base reaction
(1) $H_2O + CH_3COOH \rightleftharpoons H_3O^+ + CH_3COO^-$
(2) $2NH_3 + H_2SO_4 \rightleftharpoons 2NH_4^+ + SO_4^{2-}$
(3) $NH_3 + CH_3COOH \rightleftharpoons NH_4^+ + CH_3COO^-$
(4) $Cu^{+2} + 4NH_3 \rightleftharpoons [Cu(NH_3)_4]^{2+}$

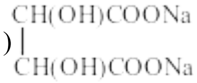
Q.87 Conjugate base of hydrazoic acid is -
(1) NH_3^- (2) N_3^- (3) N^{3-} (4) N_2^-

Q.88 NH_3 gas dissolves in water to give NH_4OH, in this reaction water acts as -
(1) An acid (2) A base
(3) A salt (4) A conjugate base

Q.89 Conjugate acid of $Zn(OH)_2$ is -
(1) $Zn(OH)^+$ (2) $Zn(OH_3)^-$
(3) Zn^{2+} (4) None

Q.90 When ammonia is added to water it decreases the concentration of which of the following ion -
(1) OH^- (2) H_3O^+ (3) NH^+_4 (4) None

Q.91 The strongest acid among the following is -
(1) $ClO_3(OH)$ (2) $ClO_2(OH)$
(3) $SO(OH)_2$ (4) $SO_2(OH)_2$

Q.92 The mixed salt among the following is -
(1) 
$\begin{array}{l} CH(OH)COONa \\ | \\ CH(OH)COONa \end{array}$
(2) $NaKSO_4$
(3) $CaCl_2$ (4) All

Q.93 Which on addition to water lowest the pH -
(1) NaCl (2) $CaCl_2$
(3) CCl_4 (4) $SiCl_4$

Q.94 For two acids A and B, $pKa_1 = 1.2$, $pKa_2 = 2.8$ respectively in value , then which is true -
(1) A and B both are equally acidic
(2) A is stronger than B
(3) B is stronger than A
(4) None of these

Q.95 Which of the following is not a Bronsted acid -
(1) $CH_3NH_4^+$ (2) CH_3COO^-
(3) H_2O (4) HSO_4^-

Q.96 Which of the following example behave as a Lewis acid BF_3, $SnCl_2$, $SnCl_4$ -
(1) Stanus chloride, stanic chloride
(2) BF_3 Stanus chloride
(3) Only BF_3
(4) BF_3, stanus chloride, stanic chloride

Q.97 In the reaction
$HNO_3 + H_2O \rightleftharpoons H_3O^+ + NO_3^-$, the conjugate base of HNO_3 is -
(1) H_2O (2) H_3O^+
(3) NO_3^- (4) H_3O^+ and NO_3^-

Q.98 The conjugate base of the weak acid in the reaction $HBr + H_2O \rightleftharpoons H_3O^+ + Br^-$ is
(1)HBr (2) H_2O (3) Br^- (4) H_3O^+

Q.99 Arrange NH_4^+, H_2O, H_3O^+, HF and OH^- increasing order of acidic nature -
(1) $OH^- < H_2O < NH_4^+ < HF < H_3O^+$
(2) $H_3O^+ > HF > H_2O > NH_4^+ > OH^-$
(3) $NH_4^+ < HF < H_3O^+ < H_2O < OH^-$
(4) $H_3O^+ < NH_4^+ < HF < OH^- < H_2O$

Q.100 In the reaction , $AlCl_3 + Cl^- \rightarrow [AlCl_4]^-$, $AlCl_3$ acts as -
(1) Salt (2) Lewis base
(3) Bronsted acid (4) Lewis acid

Q.101 Mg^{2+} is …………… than Al^{3+} -
(1) Strong Lewis acid (2) Strong Lewis base
(3) Weak Lewis acid (4) Weak Lewis base

Q.102 The two Bronsted bases in the reaction
$HC_2O_4^- + PO_4^{3-} \rightleftharpoons HPO_4^{2-} + C_2O_4^{2-}$ are
(1) $HC_2O_4^-$ and PO_4^{2-} (2) HPO_4^{2-} and $C_2O_4^{2-}$
(3) PO_4^{3-} and $C_2O_4^{-2}$ (4) $HC_2O_4^-$ and HPO_4^{2-}

Q.103 The compound HCl behaves as …. in the reaction $HCl + HF \rightleftharpoons H_2^+Cl + F^-$
(1) Strong acid (2) Strong base
(3) Weak acid (4) Weak base

Q.104 The anhydride of acid H_3PO_4 and HPO_3 are -
(1) P_2O_5 and P_2O_3 (2) P_2O_5

(3) P_2O_3 (4) None

Q.105 Which of the following is true -
(1) K_b of aniline > K_b of ethylamine
(2) pK_b of aniline > pK_b of ethylamine
(3) pK_b of aniline < pK_b of ethylamine
(4) K_b of ethylamine < K_b of aniline

Q.106 Which of the following is not a lewis base-
(1) NH_3 (2) O^{2-} (3) H_2O (4) I^+

Q.107 Which of the following is bronsted Lowry acid -
(1) SO_4^{-2} (2) H_3O^+ (3) OH^- (4) Cl^-

Q.108 The conjugated base for bicarbonate ion is -
(1) CO_3^{2-} (2) HCO_3^- (3) CO_2 (4) H_2CO_3

Q.109 Amongest the trihalides of Nitrogen which one is least basic -
(1) NBr_3 (2) NF_3 (3) NCl_3 (4) NI_3

Q.110 Conjugated base of OH^- is
(1) H_2O (2) H_3O^+ (3) H^+ (4)O^{2-}

Q.111 The Ligands in complex compounds are -
(1) Lewis bases (2) Lewis acids
(3) Bronsted acids (4) Arrhenius bases

Q.112 HCl does not behave as acid in -
(1) NH_3 (2) C_2H_5OH
(3) H_2O (4) C_6H_6

Q.113 The strongest Lewis base is -
(1) O^{-2} (2) P^{-3} (3) N^{-3} (4) F^-

Q.114 Which one of the following is the weakest base -
(1) NaOH (2) NH_4OH
(3) $Ca(OH)_2$ (4) $Ba(OH)_2$

Q.115 Which of the following is a base according to Lowry Bronsted concept -
(1) I^- (2) H_3O^+
(3) HCl (4) NH_4^+

Q.116 In which of the following reactions NH_3 acts as acid -
(1) $NH_3 + HCl \rightarrow NH_4Cl$
(2) $NH_3 + H^+ \rightarrow NH_4^+$
(3) $NH_3 + Na \rightarrow NaNH_2 + \frac{1}{2}H_2$
(4) NH_3 cannot act as acid

Q.117 According to Bronsted concept the acids in the following reaction $NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$ are -
(1) NH_3 and NH_4^+ (2) H_2O and OH^-
(3) H_2O and NH_4^+ (4) NH_3 and OH^-

Q.118 Consider the following reactions -
(i) $CO_3^{2-} + H_2O \rightleftharpoons HCO_3^- + OH^-$
(ii) $CO_2 + H_2O \rightleftharpoons H_2CO_3$
(iii) $NH_3 + H_2O \rightleftharpoons NH_4OH$
(iv) $HCl + H_2O \rightleftharpoons Cl^- + H_3O^+$
Which of the pairs of reaction proves that water is amphoteric in character :
(1) (i) and (ii) (2)(ii) and (iii)
(3) (iii) and (iv) (4) (i) and (iii)

Q.119 CH_3COO^- ions is a
(1) Weak conjugate base
(2) Strong conjugate base
(3) Weak conjugate acid
(4) Strong conjugate acid

Q.120 Which of the following is strongest conjugate base -
(1) ClO_4^- (2) HCO_3^-
(3) F^- (4) HSO_4^-

Q.121 Which of the following is not lewis base -
(1) CN^- (2) ROH (3) NH_3 (4) $AlCl_3$

Q.122 Which of the following species can act as Lewis base -
(1) Cu^{2+} (2) $AlCl_3$
(3) NH_3 (4) BF_3

Q.123 Which of the following is acid -
(1) NH_4Cl (2) $MgCl_2$
(3) CO_2 (4) H_2O

Q.124 Among the following which is not a Lewis acid -
(1) $SnCl_2$ (2) $AlCl_3$
(3) CCl_4 (4) $SiCl_4$

Q.125 Which of the following statements is correct -
(1) BCl_3 and $AlCl_3$ are both Lewis acids and BCl_3 is stronger than $AlCl_3$
(2) BCl_3 and $AlCl_3$ are both lewis acids and $AlCl_3$ is stronger than BCl_3
(3) BCl_3 and $AlCl_3$ are both equally strong Lewis acids

(4) Both BCl_3 and $AlCl_3$ are not Lewis acids

Q.126 A compound having the formula NH_2CH_2COOH may behave -
(1) Only as an acid
(2) Only as a base
(3) Both as an acid and base
(4) Neither acid nor base

Q.127 Which of the following is not a Lewis base
(1) CH_4 (2) C_2H_5OH
(3) Acetone (4) Sec. amine

Q.128 BF_3 is acid according to
(1) Lewis
(2) Arrhenius
(3) Bronsted and Lowery
(4) Madam Curie

Q.129 Which of the following can act both as Bronsted acid and Bronsted base -
(1) Na_2CO_3 (2) OH^-
(3) CO_3^{-2} (4) NH_3

Q.130 Which of the following is the strongest Lewis acid -
(1) BI_3 (2) BBr_3 (3) BCI_3 (4) BF_3

Q.131 The strongest conjugate base is -
(1) NO_3^- (2) CI^-
(3) SO_4^{2-} (4) CH_3COO^-

Q.132 Which of the following is strongest Lewis base-
(1) CH_3^- (2) NH_2^-
(3) OH^- (4) F^-

Q.133 Aluminium chloride is -
(1) Bronsted Lowry acid
(2) Arrhenius acid
(3) Lewis acid
(4) Lewis base

Q.134 Water is a -
(1) Protogenic solvent (2) Protophilic solvent
(3) Amphiprotic solvent (4) Aprotic solvent

Q.135 Ammonium ion is
(1) A conjugate acid
(2) A conjugate base
(3) Neither an acid nor a basic
(4) Both an acid and a base

Q.136 Among the following, the weakest base is -
(1) H^- (2) CH_3^- (3) CH_3O^- (4) Cl^-

Q.137 Species which do not act both as Bronsted acid and base is -
(1) $(HSO_4)^{-1}$ (2) Na_2CO_3
(3) NH_3 (4) OH^{-1}

Q.138 Which one of the following is strong Lewis base and Bronsted acid and bronsted base -
(1) NH_3 (2) PH_3 (3) CH_4 (4) BH_3

Q.139 Which one is following is strong base -
(1) NCl_3 (2) PCl_3
(3) $AsCl_3$ (4) $SbCl_3$

Q.140 Which of the following pair is Lewis acid and Lewis base and product of these is also Lewis base -
(1) BF_3, NH_3 (2) $SiCl_4$, $2Cl^-$
(3) $CH_3^{\oplus}$, $^{\ominus}OC_2H_5$ (4) None of these

Q.141 Which of the following is not correct statement
(1) Arrhenous theory of acids-bases is capable of explaining the acidic or basic nature of the substance in the solvents other than water
(2) Arrhenous theory does not explain acidic nature of $AlCl_3$
(3) The aqueous solution of Na_2CO_3 is alkaline although it does not contain OH^- ions
(4) Aqueous solution of CO_2 is acidic although it does not contain H^+ ions

Q.142 For the reaction $NH_4^+ + S^{-2} \rightleftharpoons NH_3 + HS^-$, NH_3 and S^{-2} are a group of -
(1) Acids (2) Bases
(3) Acid- base pair (4) None of these

EXERCISE # 2A

Q.1 Four solution of NH_4Cl are taken with concentrations 1M, 0.1 M, 0.01 M and 0.001 M. Their degree of hydrolysis are h_1, h_2, h_3 and h_4. What is the gradation of degree of hydrolysis ?

(1) $h_1 > h_2 > h_3 > h_4$ (2) $h_1 = h_2 = h_3 = h_4$
(3) $h_4 > h_3 > h_2 > h_1$ (4) None of these

Q.2 The solubility product of $BaCrO_4$ is 2.4×10^{-10} M^2. The maximum concentration of $Ba(NO_3)_2$ possible without precipitation in a 6×10^{-4} M K_2CrO_4 solution is-
(1) 4×10^{-7} M (2) 1.2×10^{10} M
(3) 6×10^{-4} M (4) 3×10^{-4} M

Q.3 Which of the following will occur if a 1.0 M solution of a weak acid is diluted to 0.01 M at constant temperature -
(1) Percentage ionization will increase
(2) $[H^+]$ will decrease to 0.01 M
(3) K_a will increase
(4) pH will decreases by 2 units

Q.4 Correct statement for HCN weak acid at 25ºC temperature -

(1) $\alpha = \frac{K_a}{[H^+]}$ (2) $\alpha = \frac{K_a \times [OH^-]}{K_w}$
(3) (1) and (2) both (4) $K_b = C\alpha^2$

Q.5 At 90ºC, pure water has $[H_3O^+] = 10^{-6.7}$ mol L^{-1} what is the value of K_W at 90ºC -
(1) 10^{-6} (2) 10^{-12}
(3) 10^{-67} (4) $10^{-13.4}$

Q.6 The common ion effect is shown by which of the following sets of solutions -
(1) $BaCl_2 + BaNO_3$ (2) NaCl + HCl
(3) $NH_4OH + NH_4Cl$ (4) None

Q.7 Basic strength of NH_4OH in presence of NH_4Cl
(1) Increases
(2) Remains unchanged
(3) Decreases
(4) Some times increases or sometimes decreases

Q.8 If it is known that H_2S is a weak acid and it is ionized into $2H^+$ and S^{-2}. Then in this solution HCl is added so, pH becomes less, then what will happen -
(1) Decrease in S^{-2} ion concentration
(2) Concentration of S^{-2} is not affected
(3) Increases in S^{-2} ion concentration
(4) It is not possible , to add HCl in solution

Q.9 Maximum efficiency of cationic hydrolysis will be shown by -
(1) $A\ell^{+3}$ (2) Ga^{+3} (3) $T\ell^{+1}$ (4) $T\ell^{+3}$

Q.10 $HCOO^- + H_2O \rightleftharpoons HCOOH + OH^-$ is related -

(1) $h = \sqrt{K_h}$ (2) $h = \sqrt{\frac{K_h}{C}}$

(3) $h = \sqrt{\frac{K_h}{V}}$ (4) $K_h = \sqrt{hc}$

Q.11 If pK_b for CN^- at 25° C is 4.7. The pH of 0.5 M aqueous NaCN solution is :

(1) 12 (2) 10 (3) 11.5 (4) 11

Q.12 The highest pH value is of -

(1) 0.1 M NaCl
(2) 0.1 M NH_4Cl
(3) 0.1 M CH_3COONa
(4) 0.1 M CH_3COONH_4

Q.13 A weak acid react with strong base ionization constant of weak acid is 10^{-4}. Find out equilibrium constant for this reaction -

(1) 10^{-10} (2) 10^{10} (3) 10^{-9} (4) 10^{9}

Q.14 K_a for cyano acetic acid is 3.5×10^{-3}. Then the degree of hydrolysis of 0.05 M, sodium cyano acetate solution will have the following value -

(1) 4.559×10^{-6} (2) 5.559×10^{-6}
(3) 6.559×10^{-6} (4) 7.559×10^{-6}

Q.15 In solubility of salt M_2X, QY_2 and PZ_2 equal , then the relation between their K_{sp} will be -

(1) $K_{sp}(M_2X) > K_{sp}(QY_2) > K_{sp}(PZ_2)$
(2) $K_{sp}(M_2X) = K_{sp}(QY_2) < K_{sp}(PZ_2)$
(3) $K_{sp}(M_2X) > K_{sp}(QY_2) = K_{sp}(PZ_2)$
(4) $K_{sp}(M_2X) = K_{sp}(QY_2) = K_{sp}(PZ_2)$

Q.16 The expression of solubility product of mercurous iodide is

(1) $[2\,Hg^+]^2 \times 2\,[I^-]^2$ (2) $[Hg^{++}] \times [2I^-]^2$
(3) $[\,Hg_2^{2+}] \times [I^-]^2$ (4) $[Hg^{2+}]^2 \times [I^-]^2$

Q.17 At 25ºC, required volume of water , to dissolve 1g $BaSO_4$ ($K_{sp} = 1.1. \times 10^{-10}$) will be -

(1) 820 L (2) 409.5L (3) 205 L (4) 430 L

Q.18 How many grams of CaC_2O_4 will dissolve in distilled water to make one litre saturated solution. K_{sp} of CaC_2O_4 is 2.5×10^{-9} mol^2L^{-2} and its molecular weight is 128.

(1) 0.0064 g (2) 0.0128 g
(3) 0.0032 g (4) 0.0640 g

Q.19 If the solubility of AgCl (formula mass = 143) in water at 25ºC is 1.43×10^{-4} g/100 mL of solution then the value of K_{sp} will be -

(1) 1×10^{-5} (2) 2×10^{-5}
(3) 1×10^{-10} (4) 2×10^{-10}

Q.20 One litre of saturated solution of $CaCO_3$ is evaporated to dryness, when 7.0 g of residue is left. The solubility product for $CaCO_3$ is -

(1) 4.9×10^{-3} (2) 4.9×10^{-5}
(3) 4.9×10^{-9} (4) 4.9×10^{-7}

Q.21 Correct order of solubility product is -

(1) $CaCrO_4 > SrCrO_4 > BaCrO_4$
(2) $BaCrO_4 > SrCrO_4 > CaCrO_4$
(3) $CaCrO_4 > BaCrO_4 > SrCrO_4$
(4) $SrCrO_4 > BaCrO_4 > BaCrO_4$

Q.22 M_2SO_4 (M^+ is a monovalent metal ion) has a K_{sp} of 1.2×10^{-5} at 298 K. Its maximum concentration of M^+ ion that could be attained in a saturated solution of this solid at 298 K is -

(1) 3.46×10^{-3} M (2) 2.89×10^{-2} M
(3) 2.8×10^{-3} M (4) 7.0×10^{-3} M

Q.23 K_{sp} value is more for -

(1) CuS (2) NiS (3) PbS (4) CdS

Q.24 Solubility product of $Mg(OH)_2$ is 1×10^{-11}. At what pH, precipitation of $Mg(OH)_2$ will begin from 0.1 M Mg^{2+} solution -

(1) 9 (2) 5 (3) 3 (4) 7

Q.25 What will happen if the pH of the solution of 0.001 M $Mg(NO_3)_2$ solution is adjusted to pH = 9 ($K_{sp}Mg(OH)_2 = 8.9 \times 10^{-12}$)

(1) ppt will take place
(2) ppt will not take place
(3) Solution will be saturated
(4) None of these

Q.26 A solution is a mixture of 0.06 M KCl and 0.06 M KI. $AgNO_3$ solution is being added drop by drop till AgCl starts precipitating (K_{sp} AgCl = 1×10^{-10} and K_{sp} AgI = 4×10^{-16}). The concentration of Iodide ion at this stage will be nearly equal to -

(1) 4.0×10^{-5} M (2) 2.4×10^{-7} M
(3) 2.0×10^{-8} M (4) 4×10^{-8} M

Q.27 To have more sulphide ion concentration H_2S should be passed though -

(1) 1 N HCl solution
(2) 0.01 M HCl solution
(3) A neutral solution such as water
(4) An ammonical solution

Q.28 When excess oxalic acid added to $CaCl_2$, CaC_2O_4 is precipitated and the solution still contains some unprecipitated Ca^{2+} for the reason -

(1) CaC_2O_4 is a soluble salt
(2) Oxalic acid does not ionize at all

(3) When $H_2C_2O_4$ is added to $CaCl_2$, HCl is formed which is fully ionized and thus increases the H^+ ion concentration so suppresses the ionizations of $H_2C_2O_4$ and hence the solubility product of CaC_2O_4 is not exceeded -

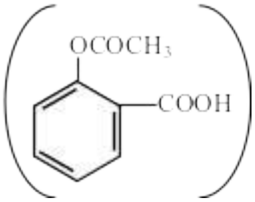
(4) None of the above

Q.29 What is the molar concentration of chloride ion for the solution obtained by mixing 300 mL of 3.0 M NaCl and 200 mL of 4.0 M solution of $BaCl_2$ -

(1) 5.0 M	(2) 1.8 M
(3) 1.6 M	(4) None of these

EXERCISE # 2B

Q.1 Acetyl salicylic acid



(mol. wr = 180) called aspirin is a pain killer with pK_a = 2. If two tables each of 0.09 gm containing aspirin are dissolved in 100 mL solution . Its pH will be -

(1) 0.5 (2) 1.0 (3) 0.0 (4) 2.0

Q.2 Which one of the following is NOT a buffer solution ?

(1) 0.8 M H_2S + 0.8 M KHS

(2) 2M $C_6H_5NH_2$ + 2M $C_6H_5N^+ H_3Br^-$

(3) 3 M H_2CO_3 + 3M $KHCO_3$

(4) 0.05 M $KClO_4$ + 0.05 M $HClO_4$

Q.3 Which of the following statements are (is) correct

(1) The pH of 1.0×10^{-8} M solution of HCl is 8

(2) The conjugate base of $H_2PO^-_4$ is HPO_4^{2-}

(3) Autoprotolysis is constant of water increases with temperature

(4) When a solution of a weak monoprotic acid is titrated against a strong base, at half neutralization point pH = 1/2 pKa

(1) a	(2) a, b
(3) a, b, d	(4) b , c

Q.4 Calculate the pH of 4×10^{-3} M, $Y(OH)_2$ solution assuming the first dissociation to be 100% second dissociation to be 50% -

(1) 11.78	(2) 9.9
(3) 2.5	(4) 2.22

Q.5 The pH of the solution produced when an aqueous solution of strong acid pH 5 is mixed with equal volume of an aqueous solution of strong acid of pH 3 is –

(1) 3.3	(2) 3.5
(3) 4.5	(4) 4

Q.6 Following five solution of KOH were prepare as

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First → 0.1 moles in 1L
Second → 0.2 moles in 2L
Third → 0.3 moles in 3L
Fourth → 0.4 moles in 4L
Firth → 0.5 moles in 5L

The pH of resultant solution is
(1) 2 (2) 1 (3) 13 (4) 7

Q.7 Which would decrease the pH of 25 cm^3 of a 0.01 M solution of hydrochloric acid -
(1) The addition of 25 cm^3, 0.005 M hydrochloric acid
(2) The addition of 25 cm^3, 0.02 M hydrochloric acid
(3) The addition of magnesium metal
(4) None

Q.8 pH of 10^{-1} M formic acid is -
(1) 1 (2) > 1 (3) < 1 (4) 13

Q.9 How many moles of HCl must be removed from 1 litre of aqueous HCl solution to change its pH from 2 to 3 -
(1) 1 (2) 0.02 (3) 0.009 (4) 0.01

Q.10 One litre solution contains 1 M HOCl [$K_a = 10^{-8}$] and 1M NaOH. What is the pH of the solution -

(1) 8 (2) 11 (3) 5 (4) 2

Q.11 The pH of 0.1 M solution of the following salts increases in order -
(1) NaCl < NH_4Cl < NaCN < HCl
(2) NaCN < NH_4Cl < NaCl < HCl
(3) HCl < NaCl < NaCN < NH_4Cl
(4) HCl < NH_4Cl < NaCl < NaCN

Q.12 To a 50 mL of 0.05M formic acid how much volume of 0.10 M sodium formate must be added to get a buffer solution pH = 4.0 ? (pK_a of the acid is 3.8)
(1) 50 mL (2) 4 mL (3) 39.6 mL (4) 100 mL

Q.13 Which can act as buffer -
(1) NH_4OH + NaOH
(2) HCOOH + CH_3COONa
(3) 40 mL 0.1 M NaCN + 20 mL of 0.1 M HCl
(4) None of these

Q.14 The H^+ ion concentration in 0.001 M acetic acid is 1.34×10^{-4} g ion L^{-1}. The H^+ ion concentration of 0.164 g of CH_3COONa is added to a litre of 0.001 M CH_3COOH will be -

(1) 9×10^{-6} (2) 18×10^{-6}
(3) 4.5×10^{-6} (4) 5×10^{-6}

Q.15 On addition of NaOH to CH_3COOH solution, 60% of the acid is neutralized. If pK_a of CH_3COOH is 4.7 then the pH of the resulting solution is -
(1) More than 4.7 but less than 5.0
(2) Less than 4.7 but more than 4.0
(3) More than 5.0
(4) Remains unchanged

Q.16 500 mL of 0.02 M acetic acid are added to 500 mL of 0.30 M sodium acetate solution . If the dissociation constant of acetic acid is 1.5×10^{-5} then pH of the resulting solution is -
(1) 5.0 (2) 9.0
(3) 3.0 (4) 4.0

Q.17 Half of the formic acid solution is neutralized on addition of a KOH solution to it. If K_a (HCOOH) = 2×10^{-4} then pH of the solution is : (log 2 = 0.3010) -
(1) 3.6990 (2) 10.3010
(3) 3.85 (4) 4.3010

Q.18 What will be the pH of the solution, if 0.01 moles of HCl is dissolved in a buffer solution containing 0.02 moles of propanoic acid ($K_a = 1.34 \times 10^{-5}$) and 0.0152 moles of salt, at at 25ºC: [log (0.173) = – 0.76]
(1) 3.11 (2) 4.11
(3) 5.11 (4) 6.11

Q.19 Calculate the pH of a buffer solution prepared by dissolving 30 g of Na_2CO_3 in 500 mL of an aqueous solution containing 150 mL of 1M HCl. Ka for HCO_3^- = 5.63×10^{-11}

$$\left[\log\left(\frac{133}{150}\right) = -0.005\right]$$

(1) 8.197 (2) 9.197
(3) 10.197 (4) 11.197

Q.20 Calculate the ratio of pH of a solution containing 1 mole of CH_3COONa + 1 mole of HCl per litre and other solution containing 1 mole CH_3COONa + 1 mole of acetic acid per litre -
(1) 1 : 1 (2) 2 : 1
(3) 1 : 2 (4) 2 : 3

Q.21 $\frac{N}{10}$ acetic acid was titrated with $\frac{N}{10}$ NaOH. When 25%, 50% and 75% of titration is over then the pH of the solution will be - [$K_a = 10^{-5}$]

(1) 5 + log 1/3, 5, 5 + log 3
(2) 5 + log 3/4, 5 + log 1/3
(3) 5 – log 1/3, 5, 5 – log 3
(4) 5 – log 1/3, 4, 5 + log 1/3

EXERCISE # 3A

Q.1 The concentration of $[H^+]$ and concentration of $[OH^-]$ of a 0.1 M aqueous solution of 2% ionised weak acid is [ionic product of water = 1×10^{-14}] - **[AIPMT -97]**

(1) 0.02×10^{-3} M and 5×10^{-11} M
(2) 1×10^{-3} M and 3×10^{-11} M
(3) 2×10^{-3} M and 5×10^{-12} M
(4) 3×10^{-2} M and 4×10^{-3} M

Q.2 When HCl gas is passed through saturated solution of common salt, pure NaCl get precipitated because - **[AIPMT -98]**

(1) In aqueous solution Cl^- obtained from dissociation of HCl which reduce the solubility product of NaCl
(2) More water is needed to dissociate HCl gas
(3) Impurities of NaCl solution dissolves in HCl
(4) Ionic product of $[Na^+][Cl^-]$ > solubility product of NaCl

Q.3 The solubility of $BaSO_4$ in water, is $2.33 \times 10^{-3} gL^{-1}$. Its solubility product will be (molecular weight of $BaSO_4$ = 233). **[AIIMS -98]**

(1) 1×10^{-5} (2) 1×10^{-10}
(3) 1×10^{-15} (4) 1×10^{-20}

Q.4 What will be the H^+ ion concentration, when 4 g NaOH dissolved in 1000 mL of water – **[AIPMT -99]**

(1) 10^{-1} (2) 10^{-13} (3) 10^{-4} (4) 10^{-10}

Q.5 Which of the following will not undergo hydrolysis in water - **[AIIMS-99]**

(1) Sodium sulphate
(2) Ammonium sulphate
(3) Calcium sulphate
(4) All the salts will hydrolyse

Q.6 Which of the following will exhibit maximum ionic conductivity - **[AIPMT -2001]**

(1) $K_4[Fe(CN)_6]$ (2) $[Co(NH_3)_6]Cl_3$
(3) $[Cu(NH_3)_4]Cl_2$ (4) $[Ni(CO)_4]$

Q.7 Ionisation constant of CH_3COOH is 1.7×10^{-5} and concentration of H^+ ions is 3.4×10^{-4}. Then find out initial concentration of CH_3COOH molecules - **[AIPMT -2001]**

(1) 3.4×10^{-4} (2) 3.4×10^{-3}
(3) 6.8×10^{-4} (4) 6.8×10^{-3}

Q.8 Solubility of a M_2S salt is 3.5×10^{-6} then find out solubility product - **[AIPMT -2001]**

(1) 1.7×10^{-6} (2) 1.7×10^{-16}
(3) 1.7×10^{-18} (4)) 1.7×10^{-12}

Q.9 The solubility product of a sparingly soluble salt AX_2 is 3.2×10^{-11}. Its solubility (in mol L^{-1}) is - **[AIPMT -2004]**

(1) 3.1×10^{-4} (2) 2×10^{-4}
(3) 4×10^{-4} (4) 5.6×10^{-6}

Q.10 When 10 mL of 0.1 M acetic acid (pKa = 5.0) is titrated against 10 mL of 0.1 M ammonia solution (pK_b = 5.0), the equivalence point occurs at pH- **[AIIMS -2004]**

(1) 5.0 (2) 6.0 (3) 7.0 (4) 9.0

Q.11 At 25ºC, the dissociation constant of base, BOH, is 1.0×10^{-12}. The concentration of hydroxyl ions in 0.01 M aqueous solution of the base would be- **[AIIMS -2005]**

(1) 1.0×10^{-6} mol L^{-1} (2) 1.0×10^{-7} mol L^{-1}
(3) 2.0×10^{-6} mol L^{-1} (4) 1.0×10^{-5} mol L^{-1}

Q.12 A weak acid HA has a K_a of 1.00×10^{-5} . If 0.100 moles of this acid is dissolved in one litre of water the percentage of acid dissociated at equilibrium is closed to - **[AIIMS -2007]**

(1) 99.0% (2) 1.00% (3) 99.9% (4) 0.100%

Q.13 Which is not a Lewis acid - **[AIPMT -91]**

(1)CCl_4 (2) $SnCl_2$ (3)$AlCl_3$ (4) BF_3

Q.14 An acid and it's conjugate base - **[AIPMT -94]**

(1) Differ by OH^- ions
(2) Differ by a proton
(3) Form salt and water
(4) Carry opposite charges

Q.15 Which of the following is a lewis acid – **[AIIMS -94]**

(1) Cl^- (2) Ag^+ (3) Br^- (4) S^-

Q.16 What volume of 0.1 M H_2SO_4 is needed to completely neutralize 40 mL of 0.2M NaOH solution - **[AIPMT -95]**

(1)10 mL (2) 40 mL (3) 20 mL (4) 80 mL

Q.17 The weakest base is - **[AIPMT -96]**

(1) KOH (2) NaOH
(3) $Zn(OH)_2$ (4) $Ca(OH)_2$

Q.18 Lewis base is - **[AIPMT -96]**

(1) $AlCl_3$ (2) BF_3
(3) NH_3 (4) NH_4^+

Q.19 The aqueous solution of which of the following salt will the lowest pH **[AIIMS -96]**

(1) NaClO (2) $NaClO_2$
(3) $NaClO_3$ (4) $NaClO_4$

Q.20 For the compound HF, HBr, H_2Se, H_2Te, H_3P which of the following statement is true - **[AIPMT -97]**

(1) HF (strong acid) (2) H_2Te (strong base)
(3) HBr (strong acid) (4) H_3P (strong base)

Q.21 In the reaction $I_2 + I^- \rightarrow I_3^-$, the Lewis base is - **[AIIMS -97]**

(1) I^- (2) I_2
(3) I_3^- (4) None of these

Q.22 The pH value of decinormal solution of NH_4OH which is 20% ionized is - **[AIPMT -98]**

(1) 13.30 (2) 14.70 (3) 12.30 (4) 12.95

Q.23 Conjugate acid of NH_2^- ions is **[AIPMT, MANIPAL -2000]**

(1) NH_4OH (2) NH_4^+
(3) NH^{-2} (4) NH_3

Q.24 Which statement is wrong about pH and H^+ **[AIPMT -2000]**

(1) pH of neutral water does not zero
(2) Adding 1N, solution of CH_3COOH and NaOH each pH will be seven
(3) pH of dilute and hot H_2SO_4 > pH of concentrate and cold H_2SO_4
(4) Mixed solution of CH_3COOH and HCl, have pH less than 7

Q.25 1M and 2.5 litre NaOH solution mixed with another 0.5 M and 3 litre NaOH solution. Then find out molarity of resultant solution - **[AIPMT -2002]**

(1) 0.80 M (2) 1.0 M
(3) 0.73 M (4) 0.50 M

Q.26 Which has highest pH - **[AIPMT -2002]**

(1) CH_3COOK (2) Na_2CO_3
(3) NH_4Cl (4) $NaNO_3$

Q.27 Solution of 0.1 N NH_4OH and 0.1 NH_4Cl has pH 9.25, Then find out pK_b of NH_4OH **[AIPMT -2002]**

(1) 9.25 (2) 4.75 (3) 3.75 (4) 8.25

Q.28 In which of the following acid -base titration, pH is greater than 8 at equivalence point **[AIIMS -2003]**

(1) Acetic acid versus ammonia
(2) Acetic acid versus sodium hydroxide
(3) Hydrochloric acid versus ammonia

(4) Hydrochloric acid versus sodium hydroxide

Q.29 Which one of the following compounds is not a protonic acid - **[AIPMT -2003]**

(1) $B(OH)_3$ (2) $PO(OH)_3$

(3) $SO(OH)_2$ (4) $SO_2(OH)_2$

Q.30 Which one of the following is NOT a buffer solution - **[AIIMS -2003]**

(1) 0.8 M H_2S + 0. M KHS

(2) 2M $C_6H_5NH_2$ + 2M $C_6H_5N^+ H_3Br$

(3) 3M H_2CO_3 + 3M $KHCO_3$

(4) 0.5M $KClO_4$ + 0.05M $HClO_4$

Q.31 Which of the following is only acidic in nature - **[AIIMS -2004]**

(1) $Be(OH)_2$ (2) $Mg(OH)_2$

(3) $B(OH)_3$ (4) $Al(OH)_3$

Q.32 The rapid change of pH near the stoichiometric point of an acid-base titration is the basis of indicator detection. pH of the solution is related to ratio of the concentrations of the conjugate acid (HIn) an base(In^-) forms of the indicator by the expression **[AIPMT -2004]**

(1) $\log \frac{[HIn]}{[In^-]} = pK_{In} - pH$

(2) $\log \frac{[HIn]}{[In^-]} = pH - pK_{In}$

(3) $\log \frac{[In^-]}{[HIn]} = pH + pK_{In}$

(4) $\log \frac{[In^-]}{[HIn]} = pK_{In} - Ph]$

Q.33 What is the pH of 0.01M glycine solution ? For glycine , $Ka_1 = 4.5 \times 10^{-3}$ and $Ka_2 = 1.7 \times 10^{-10}$ at 298 K- **[AIIMS-2004]**

(1) 3.0 (2) 10.0

(3) 6.1 (4) 7.2

Q.34 What is the correct relationship between the pHs of isomolar solutions of sodium oxide (pH_1) sodium sulphide (pH_2) sodium selenide (pH_3) and sodium telluride (pH_4) ? **[AIPMT -2005]**

(1) $pH_1 > pH_2 < pH_3 < pH_4$

(2) $pH_1 > pH_2 > pH_3 > pH_4$

(3) $pH_1 < pH_2 < pH_3 \approx pH_4$

(4) $pH_1 > pH_2 \approx pH_3 > pH_4$

Q.35 The correct order of acid strength is - **[AIPMT -2005-07]**

(1) $HClO_4 < HClO_3 < HClO_2 < HClO$

(2) $HClO_2 < HClO_3 < HClO_4 < HClO$

(3) $HClO_4 < HClO < HClO_2 < HClO_3$

(4) $HClO < HClO_2 < HClO_3 < HClO_4$

Q.36 Which of the following pair constitutes buffer - **[AIPMT -2006]**

(1) HNO_2 and $NaNO_2$ (2) NaOH and NaCl

(3) HNO_3 and NH_4NO_3 (4) HCl and KCl

Q.37 The hydrogen ion concentration of a 10^{-8} M HCl aqueous solution at 298 K ($K_w = 10^{-14}$) is - **[AIPMT -2006]**

(1) 1.0×10^{-6} M (2) 1.0525×10^{-7} M

(3) 9.525×10^{-8} M (4) 1.0×10^{-8} M

Q.38 40 mL of 0.1 M ammonia solution is mixed with 20 mL of 0.1 M HCl. What is the pH of the mixture (pK_b of ammonia solution is 4.74) **[AIIMS -2006]**

(1) 4.74 (2) 2.26 (3) 9.26 (4) 5.00

Q.39 Which of the following are present the correct order of the acidity in the given compound - **[AIPMT -2007]**

(1) $CH_3COOH > BrCH_3COOH > ClCH_2COOH > FCH_2COOH$

(2) $FCH_2COOH > CH_3COOH > FCH_2COOH > CH_3COOH$

(3) $BrCH_2COOH > ClCH_2COOH > FCH_2COOH > CH_3COOH$

(4) $FCH_2COOH > ClCH_2COOH > BrCH_2COOH > CH_3COOH$

Q.40 Calculate the pOH of a solution at 25º C that contains 1×10^{-10} M of hydronium ions, i.e. H_3O^+ **[AIPMT -2007]**

(1) 7.000 (2) 4.000 (3) 9.000 (4) 1.0000

Q.41 Equimolar solution of the following were prepared in water separately. Which one of the solution will record the highest pH? **[AIPMT -2008]**

(1) $BaCl_2$ (2) $MgCl_2$ (3) $CaCl_2$ (4) $SrCl_2$

Q.42 Equal volumes of three acid solutions of pH 3, 4 and 5 are mixed in a vessel. What will be the H^+ ion concentration in the mixture ? **[AIPMT -2008]**

(1) 3.7×10^{-4} M (2) 3.7×10^{-3} M

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(3) 1.11×10^{-3} M (4) 1.11×10^{-4} M

Q.43 If pH of a saturated solution of $Ba(OH)_2$ is 12, the value of its $K_{(SP)}$ is ? **[AIPMT -2010]**

(1) 4.00×10^{-6} M^3 (2) 4.00×10^{-7} M^3

(3) 5.00×10^{-6} M^3 (4) 5.00×10^{-7} M^3

Q.44 What is $[H^+]$ in mol/L of a solution that is 0.20 M in CH_3COONa and 0.10 M in CH_3COOH? K_a for $CH_3COOH = 1.8 \times 10^{-5}$. **[AIPMT -2010]**

(1) 3.5×10^{-4} (2) 1.1×10^{-5}

(3) 1.8×10^{-5} (4) 9.0×10^{-6}

Q.45 In a buffer solution containing equal concentration of B^- and HB, the K_b for B^- is 10^{-10}. The pH of buffer solution is – **[AIPMT -2010]**

(1) 10 (2) 7 (3) 6 (4) 4

Q.46 Which one of the following molecular hydrides acts as a Lewis acid? **[AIPMT -2010]**

(1) NH_3 (2) H_2O

(3) B_2H_6 (4) CH_4

Q.47 The tendency of BF_3, BCl_3 and BBr_3 to behave as Lewis acid decreases in the sequence - **[AIPMT -2010]**

(1) $BCl_3 > BF_3 > BBr_3$ (2) $BBr_3 > BCl_3 > BF_3$

(3) $BBr_3 > BF_3 > BCl_3$ (4) $BF_3 > BCl_3 > BBr_3$

Q.48 A buffer solution is prepared in which the concentration of NH_3 is 0.30 M and the concentration of NH_4^+ is 0.20 M. If the equilibrium constant, K_b for NH_3 equals 1.8×10^{-5}, what is the pH of this solution? (log 2.7 = 0.43) **[AIPMT -2013]**

(1) 8.73 (2) 9.08 (3) 9.43 (4) 11.72

Q,.49 In qualitative analysis, the metals of Group I can be separated from other ions by precipitating them as chloride salts. A solution initially contains Ag^+ and Pb^{2+} at a concentration of 0.10 M. Aqueous HCl is added to this solution until the Cl^- concentration is 0.10 M. What will the concentration of Ag^+ and Pb^{2+} be at equilibrium? **[AIPMT MAINS -2015]**

(K_{sp} for $AgCl = 1.8 \times 10^{-10}$,
K_{sp} for $PbCl_2 = 1.7 \times 10^{-5}$)

(1) $[Ag^+] = 1.8 \times 10^{-11}M$;
$[Pb^{2+}] = 1.7 \times 10^{-4}M$

(2) $[Ag^+] = 1.8 \times 10^{-7}M$;
$[Pb^{2+}] = 1.7 \times 10^{-6}M$

(3) $[Ag^+] = 1.8 \times 10^{-11}M$;
$[Pb^{2+}] = 8.5 \times 10^{-5}M$

(4) $[Ag^+] = 1.8 \times 10^{-9}M$;
$[Pb^{2+}] = 1.7 \times 10^{-3}M$

EXERCISE # 3B

Q.1 Solubility product of Mg $(OH)_2$ is 9×10^{-12} . If concentration of Mg^{+2} is 0.01 M then concentration of OH^- is - **[RPET -91]**

(1) 9×10^{-10} (2) 3×10^{-5}

(3) 9×10^{-12} (4) 3×10^{-7}

Q.2 Solubility of Ag_2CO_3 could be calculated by the following formula **[RPET -91]**

(1) $\sqrt{\left(\frac{K_{sp}}{8}\right)}$ (2) $\sqrt[3]{\left(\frac{K_{sp}}{4}\right)}$

(3) $\sqrt[3]{\left(\frac{K_{sp}}{2}\right)}$ (4) $\sqrt[3]{\left(\frac{K_{sp}}{8}\right)}$

Q.3 K_a for 0.1 M CH_3COOH will be, if it dissociate by 1.30% - **[RPMT -92]**

(1) 1.69×10^{-5} (2) 1.69×10^{-4}

(3) 1.69×10^{-6} (4) None of these

Q.4 Which aqueous solution having maximum pH value - **[RPMT - 92]**

(1) NaOH (2) $NaHSO_3$

(3) Na_2CO_3 (4) NaCl

Q.5 H^+ ion concentration in 0.1M NaOH is- **[RPMT -94]**

(1)10^{-1} (2) 10^{-13} (3) 10^{-2} (4) 10^{-12}

Q.6 Given K_{sp} for AgCl = 1.2×10^{-10} and K_{sp} for AgBr = 3.5×10^{-13} **[MPPET - 94]**

(1) S of AgBr < S of AgCl

(2) S of AgBr > S of AgCl

(3) S of AgBr = S of AgCl

(4) S of AgBr would be 10^6 times of AgCl

Q.7 What would be the hydrogen ion concentration of 0.006 M benzoic acid ($K_a = 6 \times 10^{-5}$) **[MPPET - 94]**

(1) 0.6×10^{-4} (2) 6×10^{-4}

(3) 6×10^{-5} (4) 3.6×10^{-4}

Q.8 Solubility product of AgCl at 100ºC is 1.44×10^{-4}, solubility of AgCl in boiling water may be - **[MPPET - 94]**

(1) 0.72×10^{-4} M (2) 1.20×10^{-2} M

(3) 0.72×10^{-2} M (4) 1.20×10^{-4} M

Q.9 Which of the following has highest pH value in water - **[AFMC -94]**

(1) NaCl (2) Na_2CO_3

(3) $NaHCO_3$ (4) KCl

Q.10 Which of the following is a strong electrolyte **[KCET -94]**

(1) NH_4OH (2) $Ca(NO_3)_2$
(3) HCN (4) H_2SO_3

Q.11 In more acidic solution, Fe(II) does not precipitate as it's sulphide. It is due to - **[RPMT -95]**

(1) High concentration of sulphide ion
(2) Low concentration of sulphide ion
(3) Acidic medium
(4) Fe (II) is not in II group

Q.12 Solubility product of PbS is 3.4×10^{-28} , if $[Pb^{+2}] = 1 \times 10^{-2}$ mol L^{-1}, then concentration of $[S^{-2}]$ for which PbS gets precipitated - **[RPMT-95]**

(1) 3.4×10^{-28} (2) 3.4×10^{-22}
(3) 3.4×10^{-26} (4) 1.0×10^{-28}

Q.13 Precipitation of CaF_2 ($K_{sp} = 1.7 \times 10^{-10}$) occurs , when …. are mixed together . **[MPPET - 95,AMU -03]**

(1) 10^{-4}M Ca^{2+} + 10^{-4} M F^{-1}
(2) 10^{-2}M Ca^{2+} + 10^{-3} M F^{-1}
(3) 10^{-2}M Ca^{2+} + 10^{-5} M F^{-1}
(4) 10^{-3}M Ca^{2+} + 10^{-5} M F^{-1}

Q.14 The precipitation occur if ionic concentration is- **[AFMC -95]**

(1) Less than solubility product
(2) More than solubility product
(3) Equal to solubility product
(4) Either '1' or '3'

Q.15 Relation between solubility and solubility product of A_xB_y type all salt is - **[RPMT -96]**

(1) $K_{sp} = x^x\, y^y\, s^{x-y}$ (2) $K_{sp} = S^{x+y}$
(3) $K_{sp} = x^y y^x S^{x+y}$ (4) $K_{sp} = x^x\, y^y\, S^{x+y}$

Q.16 Solubility of $PbCl_2$ is - **[MPPET - 96]**

(1) $\sqrt{K_{sp}}$ (2) $\sqrt[3]{K_{sp}}$
(3) $\sqrt[3]{\frac{K_{sp}}{4}}$ (4) $\sqrt{\frac{K_{sp}}{4}}$

Q.17 Degree of dissociation for a weak electrolyte is- **[MPPET - 97]**

(1) Reduce with dilution
(2) Increases with dilution
(3) Reduce or increases with dilution
(4) Not effect by dilution

Q.18 If K_{sp} for $HgSO_4$ is 6.4×10^{-5}, then solubility of the salt is - **[AFMC -97]**

(1) 8×10^{-3} (2) 8×10^{-6}
(3) 6.4×10^{-5} (4) 6.4×10^{-3}

Q.19 The pH of 10% dissociated $\frac{M}{100}$ H_2CO_3 would be - **[RPMT -98]**

(1) 2.699 (2) 3.699
(3) 3.00 (4) 0.270

Q.20 The ionization of NH_4OH is suppressed by - **[RPMT -98]**

(1) NaOH (2) NH_4Cl
(3) Both (1) and (2) (4) NaCl

Q.21 Monoacidic weak base MOH has the dissociation constant value as 1.8×10^{-5}. What would be the concentration of OH^- in its 0.1 M solution - **[RPMT -98]**

(1) 1.8×10^{-5} (2) 1.34×10^{-3}
(3) 5×10^{-5} (4) 4.0×10^{-3}

Q.22 Aqueous solution of ammonium acetate is - **[RPMT -99]**

(1) Weak acidic (2) Weakly basic
(3) Strongly acidic (4) Almost neutral

Q.23 The solubility product of $BaSO_4$ at 25ºC is 1.0×10^{-9}. What would be the concentration of H_2SO_4 necessary to precipitate $BaSO_4$ from a solution of 0.01 M Ba^{+2} ions **[RPMT -99]**

(1) 10^{-9} (2) 10^{-8} (3) 10^{-7} (4) 10^{-6}

Q.24 The hydrogen ion concentration in a solution of weak acid of dissociation constant Ka and concentration C is nearly equal to- **[RPMT-2000]**

(1) $\sqrt{K_a.C}$ (2) $\sqrt{\frac{K_a}{C}}$
(3) C/K_a (4) $K_a.C$

Q.25 At 90ºC pure water has $[H_3O^+] = 10^{-6}$ mol L^{-1}. The value of K_w at 90ºC is - **[RPMT -2000]**

(1) 10^{-6} (2) 10^{-12} (3) 10^{-14} (4) 10^{-8}

Q.26 The correct representation of solubility product of SnS_2 is - **[RPMT -2000]**

(1) $[Sn^{4+}][S^{2-}]^2$ (2) $[Sn^{4+}][S^{2-}]$
(3) $[Sn^{4+}]\,[2S^{2-}]$ (4) $[Sn^{4+}][2S^{2-}]^2$

Q.27 If the solubility product K_{sp} of a sparingly soluble salt MX_2 at 25ºC is 1.0×10^{-11}, the solubility of the salt in mol L^{-1} at this temperature will be - **[RPMT -2000]**

(1) 2.46×10^{14} (2) 1.36×10^{-4}
(3) 2.60×10^{-7} (4) 1.20×10^{-10}

Q.28 A solution of $FeCl_3$ in water acts as acidic due to - **[RPMT -2000]**

(1) Acidic impurities (2) Ionisation
(3) Hydrolysis of Fe^{3+} (4) Dissociation

Q.29 Addition of conc. HCl to saturated $BaCl_2$ solution precipitates $BaCl_2$, because - **[AMU -2000]**
(1) It follows from Le Chatelier's principle
(2) of common-ion-effect
(3) ionic product $[Ba^{++}][Cl^{-1}]$ remains constant in saturated solution
(4) At constant temperature, the product $[Ba^{2+}][Cl^-]^2$ remains constant in a saturated solution

Q.30 At 25ºC, OH^- ion concentration in 10^{-5} M HCl (aq.) will be- **[AMU -2000]**
(1) Zero (2) 10^{-9} M
(3) 10^{-5} M (4) 10^{-2} M

Q.31 The pKa of HNO_2 is 3.37. The pH of HNO_2 in its 0.01 mol L^{-1} aqueous solution will be - **[RPMT -2001]**
(1) 5.37 (2) 2.69 (3) 1.69 (4) 0.69

Q.32 If solubility product of AgCl at 25ºC is 5×10^{-13} then solubility will be- **[RPMT -2001]**
(1) 5×10^{-13} (2) 7.1×10^{-7}
(3) 2.5×10^{-13} (4) 2.5×10^{-6}

Q.33 For a solid Fe $(OH)_2$ molar solubility (S) and solubility product (Ksp) so Ksp is - **[RPMT -2001]**
(1) S (2) $4S^3$ (3) S^3 (4) None

Q.34 When add 0.01 M HCl in aqueous solution of acetic acid - **[RPMT -2001]**
(1) CH_3COO^- molar conc. is decrease
(2) CH_3COOH molar conc. is decrease
(3) CH_3COO^- molar conc. is increase
(4) NOT

Q.35 On passing H_2S gas through a solution of Cu^{+2} and Zn^{+2} ions, CuS is precipitated first because - **[AMU -2001]**
(1) Solubility product of CuS is equal to the ionic product of ZnS ;
(2) Solubility product of CuS is equal to the solubility product of ZnS
(3) Solubility product of Cus is lower than the solubility product of ZnS
(4) Solubility product of CuS is greater than the solubility product of ZnS

Q.36 The relationship between degree of ionization α and change in concentration of any weak electrolyte is represented as - **[RPMT -2002]**
(1) $\alpha = \frac{K_a}{C}$ (2) $\alpha = \sqrt{\frac{K_a}{C}}$
(3) $\alpha = K_a.C$ (4) $\alpha = \frac{\sqrt{K_a}}{C}$

Q.37 At 298 K, the solubility of $PbCl_2$ is 2×10^{-2} mol L^{-1} then k_{sp} = ? **[RPMT -2002]**
(1) 1×10^{-7} (2) 3.2×10^{-7}
(3) 1×10^{-5} (4) 3.2×10^{-5}

Q.38 Solubility of MX_2 – type electrolytes is 0.5×10^{-4} mol L^{-1} then find out k_{sp} of electrolytes **[RPMT -2002]**
(1) 5×10^{-12} (2) 25×10^{-10}
(3) 1×10^{-13} (4) 5×10^{-13}

Q.39 A solution of $MgCl_2$ in water has pH **[RPMT -2002]**
(1) < 7 (2) > 7 (3) 7 (4) 14.2

Q.40 When H_2S gas is passed through the HCl containing aqueous solutions of $CuCl_2$, $HgCl_2$, $BiCl_3$ and $CoCl_2$, it does not precipitate out **[MPPMT - 2002]**
(1) CuS (2) HgS (3) $Bi_2 S_3$ (4) CoS

Q.41 Mark the correct statement - **[MPPMT - 2002]**
(1) I group basic radicals precipitate as chloride
(2) IV group basic radicals precipitate as sulphides
(3) V group basic radicals precipitate as carbonates
(4) All the above statements are correct

Q.42 The role of NH_4Cl in group III for analysis of cations is - **[AMU - 2002]**
(1) that is acts as a catalyst
(2) that is increases the solubility of hydroxides
(3) that it lowers the OH^-concentration
(4) that is causes the precipitin of cations as chlorides

Q.43 K_{sp} of $Ca_3 (PO_4)_2$ is - **[RPMT -2003]**
(1) $[Ca^{+2}]PO_4^{-3}]^2$ (2) $[Ca^{+2}]^3 [PO_4^{-3}]^2$
(3) $[Ca^{+2}]^2[PO_4^{-3}]^3$ (4) $[Ca^{+2}] [PO_4^{-3}]$

Q.44 An acid HA has dissociated as following manner $HA \rightleftharpoons H^+ + A^-$
In has concentration 1M and pH = 5 then find out dissociation constant - **[RPMT -2003]**
(1) 1×10^{-10} (2) 1×10^{-5}
(3) 5×10^{-5} (4) 5

Q.45 Which of the following group of cations will be precipitated when passing of H_2S gas in the presence of acidic medium - **[RPMT -2003]**
(1) Cu^{+2}, Cr^{+3} (2) Zn^{+2}, Co^{+2}
(3) Cu^{+2}, Cd^{+2} (4) Al^{+3}, Cd^{+2}

Q.46 The heat of neutralization is the highest in the following case - **[AMU -2003]**
(1) a strong acid and a weak base

(2) a weak acid and a strong base
(3) a strong acid and a strong base
(4) a weak acid and a weak base

Q.47 At 25ºC [H_3O^+] in an aqueous ammonium chloride solution is 4×10^{-6} mol L^{-1}, the concentration of OH^- ions in the solution should be - **[AMU -2004]**
(1) Zero (2) 4×10^{-6} M
(3) 1×10^{-7} M (4) 2.5×10^{-9}M

Q.48 If solubility product of AB_2 is 4×10^{-12} then solubility is - **[RPMT -2004]**
(1) 4×10^{-12} (2) 10^{-12}
(3) 1×10^{-4} (4) 2×10^{-4}

Q.49 Solution of sodium carbonate is- **[RPMT -2004]**
(1) Strong acid (2) Weak base
(3) Strong base (4) weak acid

Q.50 Which of the following salt undergo hydrolysis **[RPMT -2005]**
(1) CH_3COONa (2) KNO_3
(3) NaCl (4) K_2SO_4

Q.51 Ostwald name is associated with - **[RPMT -2005]**
(1) Electrolytic dissociation
(2) Distribution law
(3) Law of mass action
(4) Catalysis

Q.52 The pH of 1M NH_4Cl (aq) at 25ºC should be - **[RPMT -2005]**
(1) zero (2) between 6 and 7
(3) 7 (4) above 7

Q.53 In a saturated solution of barium chloride, the concentration of chloride ions is double by adding conc. HCl. This will cause the concentration of bariums ions to - **[AMU -2005]**
(1) remain unchanged
(2) double
(3) change by a factor of 1/2
(4) change by a factor of 1/4

Q.54 Ionic product of water increases with - **[RPMT -2006]**
(1) Decreasing pressure
(2) Increasing H^+
(3) By mixing OH^{-1}
(4) Increasing temperature

Q.55 In III group what will be done to differentiate between Fe^{+3} and Cr^{+3} - **[RPMT -2006]**
(1) Increase the concentration of NH_4OH
(2) Increase the concentration of NH_4^+ ion
(3) Decrease the concentration of OH^-
(4) both (2) and (3)

Q.56 Aqueous solution of $Al_2(SO_4)_3$ is**[RPMT -2006]**
(1) Basic and acidic (2) Neutral
(3) Basic (4) Acidic

Q.57 An aqueous solution of $FeCl_3$ is **[RPMT -2006]**
(1) basic (2) acidic
(3) neutral (4) amphoteric

Q.58 In a saturated solution of the sparingly soluble strong electrolyte $AgIO_3$ (Moleculatr mass = 283). The equilibrium which sets in is $AgIO_{3(S)} \rightleftharpoons Ag^+_{(aq)} + IO^-_{3(aq)}$If the solubility product constant k_{sp} of $AgIO_3$ at a given temperature is 1.0×10^{-8}, what is the mass of $AgIO_3$ contained in 100 mL of its saturated solution **[AIEEE -2007]**
(1) 2.83×10^{-3} g (2) 1.0×10^{-7} g
(3) 1.0×10^{-4} g (4) 28.3×10^{-2} g

Q.59 Correct relation is **[RPMT -2007]**
(1) $pK_a \times pK_b = pK_w$ (2) $pK_a + pK_b = pK_w$
(3) $pK_a / pK_b = pK_w$ (4) $pK_a - pK_b = pK_w$

Q.60 If k_{sp} of CaF_2 in pure water is 1.70×10^{-10}, then find the solubility of CaF_2 in 0.10 M NaF solution - **[RPMT -2007]**
(1) 1.70×10^{-10} (2) 1.70×10^{-9}
(3) 1.70×10^{-8} (4) 0.10 M

Q.61 The solubility product of AgCl is 1×10^{-10}, then solubility of AgCl is - **[RPMT -2007]**
(1) 1×10^{-10} (2) 1×10^{-7}
(3) 1×10^{-5} (4) 1×10^{-8}

Q.62 To precipitate Zn in form of ZnS, Why NH_4OH is first added in the solution before H_2S gas is passed through it - **[RPMT -2007]**
(1) To convert Zn into Zn^{+2}
(2) To reduce Zinc
(3) To decrease's the dissociation of H_2S
(4) To increase the dissociation of H_2S

Q.63 Ka for CH_3COOH is 1.8×10^{-5}. Find out the percentage dissociation of 0.2M CH_3COOH in 0.1 M HCl solution **[RPMT -2008]**
(1) 0.018 (2) 0.36 (3) 18 (4) 36

Q.64 The pKa of a weak acid HA is 4.80. The pK_b of weak base BOH is 4.78. The pH of an aqueous solution of the corresponding salt BA will be - **[AIEEE-2008]**
(1) 9.58 (2) 4.79 (3) 7.01 (4) 9.22

Q.65 Conjugate acid of HPO_4^{-2} will be- **[RPET - 91 MPPMT -90]**

(1) $H_2PO_4^-$ (2) PO_4^{-3} (3) H_3PO_4 (4) HPO_4^{-2}

Q.66 Methyl orange gives ……… colour in basic medium - **[RPMT -91]**

(1) Red (2) Yellow

(3) Orange (4) Violet

Q.67 Which of the following is not Lewis acid **[RPMT - 92]**

(1) $CaCl_2$ (2) BF_3

(3) $AlCl_3$ (4) $BeCl_2$

Q.68 Methyl orange will give ....colour in acidic medium :

(1) Red (2) Yellow

(3) Blue (4) Colour less

Q.69 Which of the following is not Lewis acid :

(1) $FeCl_3$ (2) BCl_3

(3) $ZnCl_2$ (4) NH_3

Q.70 Which of the following has highest pH value with water **[AFMC -94]**

(1) NaCl (2) Na_2CO_3

(3) $NaHCO_3$ (4) KCl

Q.71 Concentrations of NH_4Cl and NH_4OH in a buffer solution are in the ratio 1 : 10 . If K_b for NH_4OH is 10^{-10}, then pH of the buffer is - **[BHU -94]**

(1) 4 (2) 5 (3) 9 (4) 11

Q.72 Weak bronsted base is - **[RPET - 94]**

(1) Br^- (2) ClO_4^- (3) NO_3^- (4) SO^{-2}

Q.73 According to Lewis concept for OH^- and H_2O- **[RPET -95]**

(1) Only OH^- is base

(2) Both are acid

(3) Both are base

(4) OH^- is acid and H_2O is base

Q.74 Lewis acid is - **[RPPMT -95]**

(1) BF_3 (2) KCN (3) NH_3 (4) CH_4

Q.75 Conjugate base of HPO_4^{-2} is - **[RPMT - 95, 2001]**

(1) PO_4^{-3} (2) HPO_4^{-2} (3) H_3PO_4 (4) $H_2PO_4^-$

Q.76 Indicator which is used in the titration of CH_3COOH and NaOH **[MPPET -95]**

(1) Methyl orange (2) Methyl red

(3) Phenolphtalein (4) Litmus

Q.77 The pH values of equimolar solution of monobasic acids A, B, C and D are 9.5, 2.5, 3.5 and 5.5 respectively. The strongest acid would be - **[AFMC -95]**

(1) A (2) B (3) C (4) D

Q.78 The pH value of a solution whose hydronium ion concentration 6.5×10^{-9} mol L^{-1} is - **[BHU - 95]**

(1) 6.21 (2) 7.21 (3) 7.75 (4) 8.21

Q.79 The relative strengths of hydrohalic acids are in the order - **[KCET -95]**

(1) HI > HCl > HBr (2) HCl > HBr > HI

(3) HI > HBr > HCl (4) HBr > HCl > HI

Q.80 The pH value of N/10 sodium hydroxide is - **[Manipal -95]**

(1) 9 (2) 10 (3) 12 (4) 13

Q.81 The indicator used for the titration of a weak base and strong acid - **[RPET - 96]**

(1) Methyl orange (2) Phenolphthalein

(3) Phenol red (4) Litmus

Q.82 Which statement is true - **[MPPMT - 96]**

(1) Conjugate base of a strong acid is strong base

(2) Conjugate base of weak acid is strong base

(3) Conjugate base of a weak acid is weak base

(4) Base and it's conjugate acid gives a neutral solution after reaction

Q.83 Highest pH (14) is given by - **[KCET -96]**

(1) 0.1M H_2SO_4 (2) 0.1 M NaOH

(3) 1N NaOH (4) 1N HCl

Q.84 Which is T-Lewis acid - **[RPET - 97]**

(1) ClF_3 (2) H_2O

(3) NH_3 (4) None of these

Q.85 According to bronsted acid is - **[RPMT -97]**

(1) Proton donor (2) Proton acceptor

(3) Amphoteric (4) Protophilic

Q.86 Strongest acid is is(Given : pK_a value) - **[MP PMT -97]**

(1) HCOOH(3.77) (2) C_6H_5COOH(4.22)

(3) CH_3COOH(4.71) (4)CH_3CH_2COOH(4.88)

Q.87 H^+ ion indicator is used in - **[MPPMT -97]**

(1) Redox titration

(2) Acid base titration
(3) Only oxidation titration
(4) Only reduction titration

Q.88 The increasing order of acid strength of following is - **[AFMC -97]**
[H_3PO_4, H_2CO_3,HCl,HI]
(1) H_3PO_4, HCl, H_2CO_3,HI
(2) H_3PO_4, H_2CO_3,HCl, HI
(3) H_2CO_3, H_3PO_4, HCl, HI
(4) None

Q.89 Which of the following is not Lewis acid - **[BHU -97]**
(1) BF_3 (2) $AlCl_3$
(3) $FeCl_3$ (4) C_2H_5ONa

Q.90 Example of Lewis acid is - **[KCET - 97]**
(1) HCOOH (2) HCl
(3) $FeCl_3$ (4) C_2H_5ONa

Q.91 When HF is dissolved in formic acid, the equilibrium established is -
$HF + HCOOH \rightleftharpoons F^- + HCOOH_2^+$
the true pair of conjugate acid base is as a [acid, conjugate acid] [Base, conjugate base] : - **[RPMT -98]**
(1) (HF, HCOOH) and ($HCOOH_2^+$, F^-)
(2) (HF, $HCOOH_2^+$) and (HCOOH, F^-)
(3) ($HCOOH_2^+$, HF) and (F^-, HCOOH)
(4) (HF,F^{-1}) and ($HCOOH_2^+$, HCOOH)

Q.92 Which of the following is the strongest acid **[AFMC -98]**
(1) CF_3COOH (2) CBr_3COOH
(3) CH_3COOH (4) CCl_3COOH

Q.93 Which among the following is the strongest acid **[Manipal-98]**
(1) HOCl (2) $HClO_2$
(3) $HClO_3$ (4) $HClO_4$

Q.94 Amines behave as - **[RPMT-2000]**
(1) Lewis bases
(2) aprotic acids
(3) Amphoteric compound
(4) Lewis acids

Q.95 Electrophiles are **[RPET - 2000]**
(1) Lewis acid (2) Lewis base
(3) Bronsted acid (4) Bronsted base

Q.96 The solvent which is neither proton donor nor proton acceptor is called **[RPMT -2000]**
(1) Amphoteric (2) Neutral
(3) Aprotic (4) Protonic

Q.97 The strongest bronsted base in the following anion is - **[KCET -2000]**
(1) ClO_4^- (2) ClO_3^-
(3) ClO_2^- (4) ClO^-

Q.98 The ionic product for water is 1×10^{-14} $mol^2\ L^{-2}$, what is the pH of a 0.001M KOH solution **[MP PET - 2001]**
(1) 10^{-11} (2) 10^{-3} (3) 3 (4) 11

Q.99 Which buffer solution out of the following will have pH> 7 - **[MP PET - 2001]**
(1) $CH_3COOH + CH_3COONa$
(2) HCOOH + HCOOK
(3) CH_3COONH_4
(4) $NH_4OH + NH_4Cl$

Q.100 Conjugate base of NH_3 is - **[RPMT -2002]**
(1) NH_4^+ (2) NH_2^+ (3) NH_2^- (4) N_2

Q.101 Which of the following is not lewis acid :
(1) $AlCl_3$ (2) $FeCl_3$
(3) BCl_3 (4) PH_3

Q.102 Indicator which is not used for titration of SA and SB - **[RPMT -2002]**
(1) MeOH (2) HPh
(3) Aniline blue (4) Starch

Q.103 Phenolphthalein is a- **[RPMT-2003]**
(1) Strong acid (2) Strong base
(3) Weak base (4) Weak acid

Q.104 Which of the following is lewis base **[RPMT -2003]**
(1) CH_3NH_2 (2) Zn^{+2}
(3) BF_3 (4) Ag^+

Q.105 Which of the following is the strongest acid **[RPMT -2003]**
(1) $Ka = 1 \times 10^{-7}$ (2) $Ka = 1 \times 10^{-5}$
(3) pKa = 9 (4) pKa = 3

Q.106 The concentration of $Ca(OH)_2$ is 0.05 M then pH - **[RPMT - 2003]**
(1) 13.0 (2) 12.7
(3) 11.2 (4) 1

Q.107 Correct order of acidic strength is **[RPMT -20003]**
(1) $HCOOH > CH_3COOH > C_2H_5COOH$
(2) $C_2H_5COOH > CH_3COOH > HCOOH$
(3) $HCOOH > C_2H_5COOH > CH_3COOH$
(4) $CH_3COOH > HCOOH > C_2H_5COOH$

Q.108 In a mixture of equimolar solutions of $NaHCO_3$ and NaOH the species present in solution shall be - **[AMU -2004]**
(1) Na_2CO_3 (2) $NaHCO_3$ + NaOH
(3) NaOH (4) $NaHCO_3 + Na_2CO_3$

Q.109 In aqueous solution if conc. of H^+ is 10^{-6} the conc. of OH^{-1} ion is - **[AMU - 2004]**

(1) 10^{-8} (2) 10^{-7}
(3) 10^{-6} (4) 5×10^{-5}

Q.110 0.015 g moles of NH_4OH and 0.025 g moles of NH_4Cl are present in a solution then pH of mixture is - **[RPMT -2004]**
(1) 9.0335 (2) 8.0335
(3) 9.665 (4) 8.665

Q.111 Which is lewis acid - **[RPMT -2004]**
(1) C_2H_4 (2) H_2O
(3) CO (4) $GaCl_3$

Q.112 Maximum pKa has - **[RPMT - 2004]**
(1) $HOClO_3$ (2) $HOClO_2$
(3) HOClO (4) HOCl

Q.113 Which of the following acts as both bronsted acid and bronsted base **[RPMT -2005]**
(1) Cl^- (2) HCO_3^-
(3) H_3O^+ (4) SO_4^{-2}

Q.114 Conjugate base of a strong acid is **[RPMT -2005]**
(1) Strong base (2) Strong acid
(3) Weak base (4) Weak acid

Q.115 HCO_3^- is a conjugate acid of - **[AMU - 2005]**
(1) H_2CO_3 (2) HCOOH
(3) CO_3^{2-} (4) CO_2

Q.116 pH – range of Methyl red indicator is – **[RPMT -2006]**
(1) 4.2 – 6.2 (2) 6.8 – 10.8
(3) 8 – 9.6 (4) 6.8 – 8.2

Q.117 Which of the following is right for diprotic acid **[RPMT - 2006]**
(1) $Ka_2 > Ka_1$ (2) $Ka_1 > Ka_2$
(3) $Ka_2 > \frac{1}{Ka_1}$ (4) $Ka_2 = Ka_1$

Q.118 Which of the following is not a conjugate acid – base - **[RPMT - 2006]**
(1) HCl, Cl^- (2) HOH, OH^-
(3) SO_4^{-2}, H_2SO_4 (4) NH_3, NH_4^+

Q.119 The pK_w of a neutral solution is 13.36. The pH of the solution shall be - **[AMU -2006]**
(1) 0.64 (2) 6.68 (3) 7.64 (4) 6.36

Q.120 An ether is - **[AMU-2006]**
(1) Lewis acid (2) Bronsted acid
(3) Lewis base (4) Arrhenius acid

Q.121 The first and second dissociation constant of an acid H_2A are 1.0×10^{-5} and 5.0×10^{-10} respectively. The overall dissociation constant of the acid will be - **[AIEEE- 2006]**
(1) 5.0×10^{15} (2) 5.0×10^{-15}
(3) 0.2×10^{5}(4) 5.0×10^{-5}

Q.122 The pKa of a weak acid (HA) is 4.5. The pOH of an aqueous buffered solution of HA in which 50% of the acid is ionized is - **[AIEEE- 2007]**
(1) 2.5 (2) 9.5 (3) 7.0 (4) 4.5

Q.123 Which one of the following is the strongest base in aqueous solution - **[AIEEE- 2007]**
(1) Aniline (2) Dimethylamine
(3) methylamine (4) trimethylamine

Q.124 pH of 1M HCl is - **[RPMT- 2007]**
(1) 1 (2) 0.1 (3)0.01 (4) 0

Q.125 50 mL solution of 0.1M CH_3COOH (pK_a = 4.73) is titrated with 0.1M NaOH solution, pH of solution when half of CH_3COOH is neutralized - **[RPMT- 2007]**
(1) 4.53 (2) 4.63 (3) 4.73 (4) 4.83

Q.126 pH of solution of 0.0005M $Ca(OH)_2$ is - **[RPMT- 2007]**
(1) 3.0 (2) –3.0 (3) 11.0 (4) 14.0

Q.127 0.001 mole of NaOH is dissolved in 100 ml of water, Then pH of solution is - **[RPMT- 2007]**
(1) 2.0 (2) – 2.0 (3) 14.0 (4) 12.0

Q.128 If pK_b of a base is 7.0, then K_a of its conjugate acid will be - **[RPMT- 2007]**
(1) 7 (2) 10^7 (3) 10^{-7} (4) 10^{-14}

Q.129 pK_a of Quinoline base is 4.88. What will be the pK_a of 0.01M solution of it - **[RPMT- 2007]**
(1) 4.88 (2) 0.01 (3) 9.12 (4) 14

Q.130 The molar solubility (in mol L^{-1}) of a sparingly soluble salt MX_4 is 's'. the corresponding solubility product is K_{SP}. 's' is given in terms of K_{SP} by the relation - **[AIEEE- 2004]**
(1) s = $(K_{SP}/128)^{\frac{1}{4}}$ (2) s = $(128K_{SP})^{\frac{1}{4}}$
(3) s = $(256K_{SP})^{\frac{1}{5}}$ (4) s = $(K_{SP}/256)^{\frac{1}{5}}$

Q.131 Solid $Ba(NO_3)_2$ is gradually dissolved in a 1.0×10^{-4} M Na_2CO_3 solution. At what concentration of Ba^{2+} will a precipitate begin to form ?
(K_{sp} for Ba CO_3 = 5.1×10^{-9}) **[AIEEE-2009]**
(1) 5.1×10^{-5} M (2) 8.1×10^{-8} M
(3) 8.1×10^{-7} M (4) 4.1×10^{-5} M

Q.132 If $[S^{2-}] = 0.6 \times 10^{-2}$ mol dm^{-3} and the solubility of $[Hg^{2+}] = [Mn^{2+}] = [Fe^{2+}] = [Zn^{2+}] = 1 \times 10^{-16}$ mol dm^{-3} , then which of the following will precipitate first in aqueous solution ? [Solubility products of HgS = 3×10^{-53}; MnS = 6×10^{-16}; FeS =1×10^{-19}; ZnS=1×10^{-22}] **[IIT-2003]**

(1) HgS (2) MnS (3) FeS (4) ZnS

Q.133 Aqueous solutions of HNO_3, KOH, CH_3COOH and CH_3COONa of identical concentrations are provided. The pair(s) of solutions which form a buffer upon mixing is(are) **[IIT-2010]**

(1) HNO_3 and CH_3COOH
(2) KOH and CH_3COONa
(3) HNO_3 and CH_3COONa
(4) CH_3COOH and CH_3COONa

Q.134 In aqueous solution the ionization constants for carbonic acid are $K_1 = 4.2\times10^{-7}$ and $K_2=4.8\times10^{-11}$ Selection the correct statement for a saturated 0.034 M solution of the carbonic acid. **[AIEEE-2010]**

(1) The concentration of H^+ is double that of CO_3^{2-}
(2) The concentration of CO_3^{2-} is 0.034 M.
(3) The concentration of CO_3^{2-} is greater than that of HCO_3^-
(4) The concentration of H^+ and HCO_3^- are approximately equal.

Q.135 Solubility product of silver bromide is 5.0×10^{-13}. The quantity of potassium bromide (molar mass taken as 120 g mol^{-1}) to be added to 1 litre of 0.05 M solution of silver nitrate to start the precipitation of AgBr is **[AIEEE-2010]**

(1) 5.0×10^{-8} g (2) 1.2×10^{-10} g
(3) 1.2×10^{-9} g (4) 6.2×10^{-5} g

Q.136 Three reactions involving $H_2PO_4^-$ are given below:

[AIEEE-2010]

(1) $H_3PO_4 + H_2O \rightarrow H_3O^+ + H_2PO_4^-$
(2) $H_2PO_4^- + H_2O \rightarrow HPO_4^{2-} + H_3O^+$
(3) $H_2PO_4^- + OH^- \rightarrow H_3PO_4 + O^{2-}$

In which of the above does $H_2PO_4^-$ act as an acid?

(1) (i) Only (2) (ii) Only
(3) (iii) and (ii) (4) (iii) only

Q.137 The correct order of increasing basicity of the given conjugate bases $(R = CH_3)$ is **[AIEEE-2010]**

(1) $RCO\overline{O} < HC\equiv\overline{C} < \overline{N}H_2 < \overline{R}$
(2) $RCO\overline{O} < HC\equiv\overline{C} < \overline{R} < \overline{N}H_2$
(3) $\overline{R} < HC\equiv\overline{C} < RCO\overline{O} < \overline{N}H_2$
(4) $RCO\overline{O} < \overline{N}H_2 < HC\equiv\overline{C} < \overline{R}$

Q.138 At 25°C, the solubility product of $Mg(OH)_2$ is 1.0×10^{-11}. At which pH, will Mg^{2+} ions start precipitating in the form of $Mg(OH)_2$ from a solution of 0.001 M Mg^{2+} ions ? **[AIEEE-2010]**

(1) 8 (2) 9 (3) 10 (4) 11

Q.139 An acid HA ionise as

$HA \rightleftharpoons H^+ + A^-$

The pH of 1.0 M solution is 5. Its dissociation constant would be - **[AIEEE-2011]**

(1) 5 (2) 5×10^{-8}
(3) 1×10^{-5} (4) 1×10^{-10}

Q.140 The K_{sp} for $Cr(OH)_3$ is 1.6×10^{-30}. The molar solubility of this compound in water is - **[AIEEE-2011]**

(1) $\sqrt[4]{1.6\times10^{-30}}$ (2) $\sqrt[4]{1.6\times10^{-30}/27}$
(3) $1.6 \times 10^{-30}/27$ (4) $\sqrt[2]{1.6\times10^{-30}}$

EXERCISE # 4

(ASSERTION AND REASON TYPE)

These questions consist of two statements each, printed as Assertion and Reason. While answering these Questions you are required to choose any one of the following four responses.

(A) If both Assertion & Reason are true & the Reason is a correct explanation of the Assertion

(B) If both Assertion & Reason are True but Reason is not a correct explanation of the Assertion

(C) If Assertion is True but the Reason is False

(D) If both Assertion & Reason are False

Q.1 **Assertion : -** When small amount of acid or base is added to pure water, its pH undergoes a change .

Reason :- Addition of an acid or base increase the degree of ionization of water.

(1) A (2) B (3) C (4) D

Q.2 **Assertion : -** A very dilute acidic solution of Cd^{2+} and Ni^{2+} gives yellow precipitate of CdS on passing hydrogen sulphide.

Reason :- Solubility product of CdS is more than that of NiS.

(1) A (2) B (3) C (4) D

Q.3 **Assertion : -** The pH of an aqueous solution of acetic acid remains unchanged on the addition of sodium acetate.

Reason :- The ionization of acetic acid is suppressed by the addition of sodium acetate.

(1) A (2) B (3) C (4) D

Q.4 **Assertion : -** If HCl gas is passed through saturated NaCl solution, solid NaCl starts to precipitate.

Reason :- HCl decreases the solubility product of NaCl.

(1) A (2) B (3) C (4) D

Q.5 **Assertion : -** Heat of ionization of water is equal to the heat of neutralization of a strong acid with a strong base.

Reason :-Water ionizes to a very small extent while H^+ ions from acid combine very rapidly with OH^- from base to form H_2O.

(1) A (2) B (3) C (4) D

Q.6 **Assertion : -** Both ZnS and MnS are insoluble in dilute HCl.

Reason :- Both ZnS and MnS are insoluble in dilute HCl.

(1) A (2) B (3) C (4) D

Q.7 **Assertion : -** To precipitate the cations of fourth group in qualitative analysis , medium is made alkaline before passing H_2S gas.

Reason :- This is done to suppress the ionization of H_2S.

(1) A (2) B (3) C (4) D

Q.8 **Assertion : -** When an acid or a base is added to water at constant temperature the pH changes.

Reason :- This is due to change in ionic product of water.

(1) A (2) B (3) C (4) D

Q.9 **Assertion : -** Addition of silver ions to a mixture of aqueous sodium chloride and sodium bromide solution will first precipitate AgBr rather than AgCl.

Reason :- Ksp of AgCl < Ksp of AgBr.

(1) A (2) B (3) C (4) D

Q.10 **Assertion : -** $BaCO_3$ is more soluble in HNO_3 than in plain water.

Reason :- Carbonate is a weak base and reacts with the H^+ from the strong acid causing the barium salt to dissociate.

(1) A (2) B (3) C (4) D

Q.11 **Assertion : -** Addition of NH_4OH to an aqueous solution of $BaCl_2$ in the presence of NH_4Cl(excess) precipitates $Ba(OH)_2$

Reason :- $Ba(OH)_2$ is insoluble in water

(1) A (2) B (3) C (4) D

Q.12 **Assertion : -** Sb(III) is not precipitated as sulphide when in its alkaline solution H_2S is passed.

Reason :- The concentration of S^{2-} ion in alkaline medium is inadequate for precipitation.

(1) A (2) B (3) C (4) D

Q.13 **Assertion :** A mixture of a weak acid CH_3COOH and sodium acetate forms a buffer solution.

Reason : A buffer solution reacts with small quantities of hydrogen or hydroxyl ions and keeps the pH almost same.

(1) A (2) B (3) C (4) D

Q.14 **Assertion :** At 25ºC the pH of 10^{-8} M HCl is 8.

Reason : pH of acidic solution is always below 7 at 25ºC.

(1) A (2) B (3) C (4) D

Q.15 **Assertion :** In the acid base titration involving a strong base and a weak acid methyl orange can be used as an indicator.

Reason : Methyl orange change its colour in pH range 3 to 5.

(1) A (2) B (3) C (4) D

Q.16 **Assertion :** pH of a buffer change with temperature.

Reason : Ionic product of Water (K_w) changes with temperature.

(1) A (2) B (3) C (4) D

Q.17 **Assertion :** H_3PO_3 is a dibasic compound.

Reason : The two H-atom are directly attached to P.

(1) A (2) B (3) C (4) D

Q.18 **Assertion :** Boric acid bebaves as a weak monobasic acid.

Reason : Boric acid contains hydrogen bonds is its structure.

(1) A (2) B (3) C (4) D

Q.19 **Assertion :** H_2O is amphoteric in nature.

Reason : H_2O can accept a proton to from H_3O^+ ion and can donate a proton to form OH^- ion.

(1) A (2) B (3) C (4) D

Q.20 **Assertion :** All Arrhenius acids are also Bronsted acids.

Reason : All Bronsted bases are also lewis bases.

(1) A (2) B (3) C (4) D

Q.21 **Assertion :** The buffer solution has a capacity to resist the change in pH value on addition of small amount of acid or base to it.
Reason : pH value of buffer solution does not change on dilution or on keeping for long.
(1) A (2) B (3) C (4) D

Q.22 **Assertion :** The species in the buffer must not react with each other.
Reason : The pH of a buffer depends on the value of K_a of the weak acid and the relative concentration of that acid and its conjugate base.
(1) A (2) B (3) C (4) D

Q.23 **Assertion :** Only a very small amount of indicator should be used.
Reason : So that addition of the indicator does not effect the pH of the solution.
(1) A (2) B (3) C (4) D

Q.24 **Assertion :** An aqueous solution of ammonium acetate can act as buffer .
Reason :- An aqueous solution of any pure salt acts as a buffer .
(1) A (2) B (3) C (4) D

Q.25 **Assertion :** A solution containing acetic acid and sodium acetate in a equimolar quantities can act as a buffer solution.
Reason : The pH of the above mentioned buffer would be equal to pK_a of acetic acid.
(1) A (2) B (3) C (4) D

Q.26 **Assertion :** H_2SO_4 is a strong acid.
Reason : H_2SO_4 undergoes almost complete ionization is aqueous solution.
(1) A (2) B (3) C (4) D

Q.27 **Assertion :** Solubility of AgCl in water decrease in the presence of sodium chloride.
Reason : Sodium chloride undergoes hydrolysis in water.
(1) A (2) B (3) C (4) D

Q.28 **Assertion :** At higher temperature, K_w of water remains unaltered.
Reason : K_w is constant.
(1) A (2) B (3) C (4) D

Q.29 **Assertion :** HCl, HNO_3 and H_2SO_4 are equally strong acids in water.
Reason : Water is a stronger acid than alcohols.
(1) A (2) B (3) C (4) D

Q.30 **Assertion :** Solution of CH_3COONH_4 is a buffer solution.
Reason : H^+ ion added will be consumed by CH_3COO^- ion and OH^- ion added will be consumed by NH_4^+ ion.
(1) A (2) B (3) C (4) D

Q.31 **Assertion :** Ksp is a constant value for any salt, at particular temperature
Reason : Solubility of any salt is constant at a particular temperature.
(1) A (2) B (3) C (4) D

Q.32 **Assertion :** H_3O^+ ion from water is also taken in consideration while calculating the pH of very dilute solution (say concentration = 10^{-9} M) of acid.
Reason : $[H_3O^+]$ from water is only available in very dilute solution of acid.
(1) A (2) B (3) C (4) D

EXERCISE # 5

(NCERT QUESTIONS)

Q.1 The ionization constant of phenol is 1.0×10^{-10}. What is the concentration of phenate ion in 0.05 M solution of phenol? What will be its degree of ionization if the solution is also 0.01 M in sodium phenate ?

Sol

$$C_6H_5OH \rightleftharpoons C_6H_5O^- + H^+$$

At initial $\quad 0.05\ M \quad 0 \quad 0$

After dissociation $\quad 0.05 - x \quad x \quad x$

$$\therefore\ K_a = \frac{[C_6H_5O^-][H^+]}{[C_6H_5OH]} = \frac{(x)(x)}{0.05 - x} = 1.0 \times 10^{-10} \text{ (given)}$$

or $\frac{x^2}{0.05} = 1 \times 10^{-10}$ [x << 1,

So taking $0.05 - x \approx 0.05$ M]

$\Rightarrow \quad x^2 = 5 \times 10^{-12}$

$\Rightarrow \quad x = 2.2 \times 10^{-6}$ M

$\therefore \quad [C_6H_5O^-] = 2.2 \times 10^{-6}$

In presence of 0.01 M C_6H_5ONa let y is the amount of phenol dissociated, then at equilibrium.

$[C_6H_5OH] = 0.05 - y \approx 0.05$ M and

$[C_6H_5O^-] = 0.01 + y \approx 0.01$ M

$[H^+] = y$M

$$\therefore \quad K_a = \frac{(0.01)(y)}{0.05} = 1.0 \times 10^{-10} \text{(given)}$$

$\Rightarrow \quad y = 5 \times 10^{-10}$ M

$$\therefore \quad \alpha = \frac{y}{c} = \frac{5 \times 10^{-10}}{5 \times 10^{-2}} = 10^{-8}$$

Q.2 The first ionization constant of H_2S is 9.1×10^{-8}. Calculate the concentration of HS^- ion in its 0.1M in HCl also. If the second dissociation constant of H_2S is 1.2×10^{-13}. Calculate the concentration of S^{2-} under both condition.

Sol

$$H_2S \rightleftharpoons H^+ + H^-$$

An initial $\quad 0.1M \quad 0 \quad 0$

After disso. $\quad 0.1 - x \approx 0.1 \quad x \quad x$

$$\therefore\ K_a = \frac{[H^+][HS^-]}{[H_2S]} = \frac{x \times x}{0.1} = 9.1 \times 10^{-8} \text{ (given)}$$

$\Rightarrow \quad x^2 = 9.1 \times 10^{-9}$

$\Rightarrow \quad x = 9.54 \times 10^{-5}$ M

$\Rightarrow \quad [HS^-] = 9.54 \times 10^{-5}$ M

In presence of 0.1 M HCl, suppose H_2S dissociated is y. Then at equilibrium

$[H_2S] = 0.1 - y \approx 0.1$ M

$[H^+] = 0.1 + y \approx 0.1$ M

$[HS^-] = y$M

$$\text{Now} \quad K_a = \frac{0.1 \times y}{0.1} = 9.1 \times 10^{-8} \text{ (given)}$$

$\Rightarrow \quad y = 9.1 \times 10^{-8}$ M

$\Rightarrow \quad [HS^{-1}] = 9.1 \times 10^{-8}$ M

To calculate $[S^{-2}]$

$$H_2S \rightleftharpoons H^+ + HS^-$$

$$HS^- \rightleftharpoons H^+ + S^{-2}$$

for overall reaction,

$$H_2S \rightleftharpoons 2H^+ + S^{-2}$$

$K_a = K_{a1} \times K_{a2} \times 9.1 \times 10^{-8} \times 1.2 \times 10^{-13}$

(K_{a2} and K_{a2} are given.

$\Rightarrow \quad K_a = 1.092 \times 10^{-20}$

$$\Rightarrow \quad K_a = \frac{[H^+]^2[S^{-2}]}{[H_2S]}$$

In the absence of 0.1 M HCl

$[H^+] = 2[S^{-2}]$

Hence if $\quad [S^{-2}] = x$ M, $[H^+] = 2x$M

$$\therefore \quad K_a = \frac{(x)(2x)^2}{0.1} = 1.092 \times 10^{-20}$$

$\Rightarrow \quad 4x^3 = 1.092 \times 10^{-21}$

$\Rightarrow \quad x^3 = 0.273 \times 10^{-21} = 273 \times 10^{-24}$

taking both sides log

$3 \log x = \log 273 - 24$

[log A.B = log A + log B]

$= 2.4362 - 24$

$\Rightarrow \quad \log x = 0.8127 - 8 = \bar{8}.8217$

or $\quad x = \text{Antilog } \bar{8}.\ 8217$

$= 6.497 \times 10^{-8} = 6.5 \times 10^{-8}$ M

II case :

In presence of 0.1 M HCl

Let $\quad [S^{-2}] = y$M then

$[H_2S] = 0.1 - y \approx 0.1$ M

$[H^+] = 0.1 + y \approx 0.1$ M

$$\Rightarrow \quad K_a = \frac{[H^+]^2[S^{-2}]}{[H_2S]} = \frac{(0.1)^2(y)}{0.1} = 1.09 \times 10^{-20}$$

$\Rightarrow \quad y = 1.09 \times 10^{-19}$ M

$[S^{-2}] = 1.09 \times 10^{-19}$ M

Q.3 Assuming complete dissociation calculate the pH of the following solutions.

(1) 0.003 M HCl $\quad$ (2) 0.005 M NaOH

(3) 0.002 M HBr $\quad$ (4) 0.002M KOH

Sol (1) 0.003 M HCl $\quad$ pH = ?

$HCl \rightleftharpoons H^+ + Cl^-$ given complete dissociation

$[H^+] = 0.003 = 3 \times 10^{-3}$ M

$pH = -\log [H^+] = -[\log (3 \times 10^{-3})]$

$= -[\log 3 - 3 \log 10]$

$= 3 - \log 3 = 3 - 0.47 = 2.52$

(2) 0.005 M NaOH

$$NaOH \rightleftharpoons Na^+ + OH^-$$

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$[OH^-] = 0.005 = 5 \times 10^{-3}$ M

$\therefore$ pOH = – log $[OH^-]$

$= -[\log (5 \times 10^{-3})] = -[\log 5 - 3 \log 10)]$

$= 3 - \log 5 = 3 - 0.691 = 2.30$

We know pH + pOH = 14

$\therefore$ pH = 14 – 2.30 = 11.70

(3) 0.002 M HBr

$HBr \rightleftharpoons H^+ + Br^-$

$[H^+] = 0.002 = 2 \times 10^{-3}$ M

$\therefore$ pH = – log $[H^+]$

$= -\log [H^+]$

$= -[\log(2 \times 10^{-3}] = -[\log 2 - 3 \log 10]$

$= 3 - \log 2$

pH = 3 – 0.3010 = 2.698 ≈ 2.70

(4) 0.002 M KOH

$KOH \rightleftharpoons K^+ + OH^-$

$[OH^-] = 0.002 = 2 \times 10^{-3}$ M

$\therefore$ pOH $= -\log [OH^-] = -\log (2 \times 10^{-3})]$

$= -[\log 2 - 3\log 10] = 3 - \log 2$

$= 3 - 0.3010 = 2.70$

We know pH + pOH = 14

$\therefore$ pH = 14 – 2.70 = 11.30

Q.4 If 0.561 gram KOH is dissolved in water to given 200 mL of solution at 298 K. Calculate the concentration of potassium, hydrogen and hydroxyl ions. What is its pH?

Sol Molarity = $\dfrac{\text{No. of moles of solute}}{\text{Volume of solution (litre)}}$

$= \dfrac{0.561 \times 1000}{56 \times 200} = 0.05$ M

$KOH \rightleftharpoons K^+ + OH^-$

We know KOH is a strong electrolyte and completely dissociated and concentration of K^+ and OH^- will be equal.

So $[K^+] = [OH^-] = 0.05$ M

and $[H^+] = \dfrac{10^{-14}}{0.05} = 2 \times 10^{-13}$ M

pH $= -\log[H^+] = -\log 2 \times 10^{-13}$

$= 13 - \log 2 = 13 - 0.3010 \approx 12.7$

Q.5 The ionization constant of propanoic acid is 1.32×10^{-5} . Calculate the degree of ionization of the acid in its 0.05 M solution and also its pH. What will be its degree of ionization if the solution is 0.01M in HCl also?

Sol $CH_3CH_2COOH \rightleftharpoons CH_3\,CH_2COO^- + H^+$

c	0	0
c – cα	cα	cα

$\therefore\ K_a = \dfrac{c^2\alpha^2}{c(1-\alpha)}$,

$K_a = \alpha^2 C$ $\qquad 1 - \alpha \approx 1$

$\therefore\ \alpha = \sqrt{\dfrac{K_a}{c}} = \sqrt{\dfrac{1.32 \times 10^{-5}}{0.05}} = 1.62 \times 10^{-2}$

given c = 0.05

$[H^+] = C\alpha$

$= 5 \times 10^{-2} \times 1.62 \times 10^{-2} = 8.10 \times 10^{-4}$ M

pH $= -\log [H^+]$

$= -\log (8.10 \times 10^{-4}) = 4 - \log 8.1$

$= 4 - 4 \log 3 + \log 10 = 4 - 4(0.47) + 1$

$= 5 - 1.88 = 3.12$

If c is the initial concentration and x is the amount now dissociated then at equilibrium .

$[CH_3CH_2COOH] = c - x$M

$[CH_3CH_2COO^-] = x$M, $[H^+] = 0.01 + x$M

$\therefore\ K_a = \dfrac{x(0.01 + x)}{c - x} = \dfrac{x(0.01)}{c}$

$\Rightarrow\ \dfrac{x}{c} = \dfrac{K_a}{0.01} = \dfrac{1.32 \times 10^{-5}}{10^{-2}} = 1.32 \times 10^{-3}$

$\therefore\ \alpha = 1.32 \times 10^{-3}$

Q.6 The pH of 0.1 M solution of cyanic acid (HCNO) is 2.34. Calculate the ionization constant of the acid and its degree of ionization in the solution.

Sol $HCNO \rightleftharpoons H^+ + CNO^-$

given pH = 2.34

$-\log H^+] = 2.34 \Rightarrow \log [H^+] = -2.34$

$\Rightarrow\ [H^+] = 10^{-2.34}$ M

$\Rightarrow\ [H^+] = 4.57 \times 10^{-3}$ M

$[CNO^-] = [H^+] = 4.57 \times 10^{-3}$M

and $K_a = \dfrac{[H^+][CNO^-]}{[HCNO]}$

$= \dfrac{(4.57 \times 10^{-3})(4.57 \times 10^{-3})}{0.1} = 2.09 \times 10^{-4}$

and we know

$\alpha = \sqrt{\dfrac{K_a}{c}} = \sqrt{\dfrac{2.09 \times 10^{-4}}{0.1}} = 0.0457$

Q.7 The ionization constant of nitrous acid is 4.5×10^{-4}. Calculate the pH of 0.04 sodium nitrite solution and also its degree of hydrolysis.

Sol given $K_a = 4.5 \times 10^{-4}$

Sodium nitrite is a salt of strong base and weak acid

$\therefore\ K_h = \dfrac{K_w}{K_a} = \dfrac{10^{-14}}{(4.5 \times 10^{-4})}\quad 2.22 \times 10^{-11}$

$h = \sqrt{\dfrac{K_h}{C}} = \sqrt{\dfrac{2.22 \times 10^{-11}}{0.04}} = \sqrt{5.5 \times 10^{-10}}$

$= 2.36 \times 10^{-5}$

$[OH^-] = \sqrt{K_h C} = \sqrt{2.22 \times 10^{-11} \times 0.04}$

$= \sqrt{8.80 \times 10^{-13}} = 9.42 \times 10^{-7}$ M

$\therefore$ pOH $= -\log [OH^-]$
$= -\log [9.42 \times 10^{-7}] = 7 - 0.9714 = 6.03$
$\therefore$ pH $= 14 - pOH = 14 - 6.03 = 7.97$
where h = degree of hydrolysis

Q.8 A 0.02 M solution of pyridinium hydrochloride has pH = 3.44. Calculate the ionization constant of pyridine.

Sol Pyridine hydrochloride is a salt of weak base and strong acid hence.

$$pH = -\frac{1}{2}[\log K_w - \log K_b + \log c]$$

$$\Rightarrow \quad 3.44 = -\frac{1}{2}[-14 - \log K_b + \log 2 \times 10^{-2}]$$

(given pH = 3.44, C = 0.02)
$\Rightarrow \quad 6.88 = 14 + \log K_b + 1.70$
$\Rightarrow \quad \log K_b = -8.82 \Rightarrow K_b$
$= 10^{-8.82} \Rightarrow K_b = 1.5 \times 10^{-9}$

Q.9 Predict if the solutions of the following salts are neutral , acidic or basic -
NaCl, KBr, NaCN, NH_4NO_3, $NaNO_2$ and KF.

Sol NaCN, $NaNO_2$, KF solutions are basic. Because these are the salts of strong base and weak acid.
NaCl, KBr solutions are neutral. Because salts of strong base.
NH_4NO_3 solution is acidic because salts of strong acid and weak base.

Q.10 The ionization constant of chloroacetic acid is 1.35×10^{-3}. What will be pH of 0.1 M acid and its 0.1 M sodium salt solution.

Sol We know chloroacetic acid is a weak acid.
Hence $[H^+] = \sqrt{K_a \times c}$ given
$K_a = 1.35 \times 10^{-3}$, c = 0.1 M
$= \sqrt{1.35 \times 10^{-3} \times 0.1} = 1.16 \times 10^{-2}$ M
$\therefore$ pH $= -\log [H^+] = -\log [1.16 \times 10^{-2}]$
$= 2 - 0.06 = 1.94$
$\therefore$ pH of acid solution = 1.94
Sodium salt of chloroacetic acid is a salt of strong base and weak acid.
Hence ,

$$pH = -\frac{1}{2}[\log K_w + \log K_a - \log C]$$

$$= -\frac{1}{2}[-14 + \log(1.35 \times 10^{-3}) - \log 10^{-1}]$$

$\therefore$ pH of its salt solution = 7.94

Q.11 Ionic product of water at 310 K is 2.7×10^{-14}. What is pH of neutral water at this temperature ?

Sol $K_w = [H^+][OH^-] = 2.7 \times 10^{-14}$
for neutral water $[H^+] = [OH^-]$
$\therefore \quad [H^+] = \sqrt{2.7 \times 10^{-14}} = 1.64 \times 10^{-7}$ M
$\therefore \quad pH = -\log [H^+] = -\log [1.64 \times 10^{-7}]$

pH = 6.81

Q.12 What is the maximum concentration of equimolar solutions of ferrous sulphate and sodium sulphide so that when mixed in equal volumes, there is no precipitation of iron sulphide . For iron sulphide $K_{sp} = 6.3 \times 10^{-18}$.

Sol Let the concentration of ferrous sulphate ($FeSO_4$) and sodium sulphide (Na_2S) is y mol L^{-1}. Then after mixing equal volumes (given)

$$[FeSO_4] = [Na_2S] = \frac{y}{2} M$$

i.e. $[Fe^{+2} = [S^{-2}] = \frac{y}{2}$ M

K_{sp} for iron sulphide (FeS) $= [Fe^{+2}][S^{-2}]$

i.e. $6.3 \times 10^{-18} = \frac{y}{2} \times \frac{y}{2}$ (given)
$\Rightarrow \quad y^2 = 4 \times 6.3 \times 10^{-18}$
$\therefore \quad y = \sqrt{4 \times 6.3 \times 10^{-18}}$ M
$= 5.02 \times 10^{-9}$ M

Q.13 What is the minimum volume of water required to dissolve 1 g of calcium sulphate at 298 K. For calcium sulphate K_{sp} is 9.1×10^{-6}.

Sol $CaSO_4(s) \rightleftharpoons Ca^{+2}(aq.) + SO_4^{-2}(aq.)$
If S is the solubility of $CaSO_4$ in moles L^{-1} then.
$K_{sp} = [Ca^{+2}]\ [SO_4^{-2}]$
$= S \times S = S^2 \quad K_{sp} = 9.1 \times 10^{-6}$ (given)
$\Rightarrow \quad S = \sqrt{K_{sp}} = \sqrt{9.1 \times 10^{-6}}$ M
$\Rightarrow \quad S = 3.02 \times 10^{-3}$ mol L^{-1}
[Molar mass $CaSO_4$ = 136 g mol^{-1}]
$= 3.02 \times 10^{-3} \times 136$ g L^{-1} = 0.411 g:$^{-1}$
So for dissolving 0.411 g, water required = 1L
$\therefore$ for dissolving 1 g, water required

$$= \frac{1}{0.411} \times 1 = 2.43 \text{ L}$$

Q.14 The concentration of sulphide ion in 0.1 M HCl solution saturated with hydrogen sulphide is 1.0×10^{-19} M. If 10 mL of this is added to 5 mL of 0.04 M solution of the following : $FeSO_4$, $MnCl_2$, $ZnCl_2$ and $CdCl_2$. In which solution precipitation will take place.
ZnS = $K_{sp} = 1.6 \times 10^{-24}$ MnS = $K_{sp} = 2.5 \times 10^{-13}$
FeS = $K_{sp} = 6.3 \times 10^{-18}$ CdS = 8.0×10^{-27}

Sol We know when ionic product is greater than solubility product precipitation will take place in the solution . Given that as 10 mL of solution containing S^{-2} ion is mixed with 5 mL of metal salts solution after mixing.

$$[S^{-2}] = 1.0 \times 10^{-19} \times \frac{10}{15} = 6.67 \times 10^{-20} M$$

$$[Fe^{+2}] = [Mn^{+2}] = [Zn^{+2}] = [Cd^{+2}]$$

$$= \frac{5}{15} \times 0.04 = 1.33 \times 10^{-2}\text{M}$$

Hence ionic product for each of these will be .
$= [M^{+2}]\,[S^{-2}]$
$= [1.33 \times 10^{-2}]\,[6.67 \times 10^{-20}] = 8.87 \times 10^{-22}$

As this is greater than the solubility product of ZnS and CdS therefore , $ZnCl_2$ and $CdCl_2$ solution will be precipitated

Q.15 Calculate the pH of the following solutions -
(1) 2g of TlOH dissolved in water to given 2 litre of solution.
(2) 0.3 g of $Ca(OH)_2$ dissolved in water to give 500 mL of solution.

Sol (1) $[\text{TlOH}] = \dfrac{2}{221.37 \times 2} = 4.517 \times 10^{-3}$ M
$\therefore$ pOH $= -\log[OH^-] = -\log 4.517 \times 10^{-3} = 2.3452$
$\therefore$ pH $= 11.6548$
(2) $[Ca(OH)_2] = \dfrac{0.3 \times 1000}{74 \times 500} = 8.108 \times 10^{-3}$ M
$\therefore$ $[OH^-] = 2 \times 8.108 \times 10^{-3}$M
$\therefore$ pOH $= -\log[OH^-] = -\log 16.216 \times 10^{-3}$
$= 1.7900$
$\therefore$ pH $= 12.21$

Q.16 Calculate the hydrogen ion concentration in the following biological fluids whose pH are given below.
(1) Human muscle-fluid 6.83
(2) Human stomach fluid 1.2
(3) Human blood 7.38
(4) Human saliva 6.4

Sol (1) pH = 6.83 or $-\log[H^+] = 6.83$
$\therefore$ $[H^+] = 1.479 \times 10^{-7}$M
(2) pH = 1.2 or $-\log[H^+] = 1.2$
$\therefore$ $[H^+] = 6.31 \times 10^{-2}$ M
(3) pH= 7.38 or $-\log[H^+] = 7.38$
$\therefore$ $[H^+] = 4.17 \times 10^{-8}$ M
(4) pH = 6.4 or $-\log[H^+] = 6.4$
$[H^+] = 3.98 \times 10^{-7}$M

Q.17 The solubility of $Sr(OH)_2$ at 298 K is 19.23 gL^{-1} of solution. Calculate the concentrations of strontium and hydroxyl ions and the pH of solution.

Sol $[Sr(OH)_2] = \dfrac{19.23}{121.62 \times 1} = 0.158$ M
$\therefore$ $[OH^-] = 2 \times 0.158$ M $= 0.316$ M
or pOH = 0.5003
pH = 13.4997
$\therefore$ $[Sr^{2+}] = 0.158$ M

Q.18 The solubility product of Ag_2CrO_4 and AgBr are 1.1×10^{-12} and 5.0×10^{-13} respectively. Calculate the ratio of the molarities of their saturated solutions.

Sol
$$Ag_2CrO_2 \rightleftharpoons \underset{2x}{2Ag^+} + \underset{x}{CrO_4^{2-}}$$

Let x be solubility of Ag_2CrO_2
$$AgBr \rightleftharpoons \underset{y}{Ag^+} + \underset{y}{B^-}$$

Let y be solubility of AgBr

For Ag_2CrO_4 : $K_{sp} = 4x^3$
$$x = \sqrt[3]{\frac{K_{sp}}{4}} = \sqrt[3]{\frac{1.1 \times 10^{-12}}{4}} = 6.5 \times 10^{-5}\text{ M}$$

For AgBr : $K_{sp} = y^2$
$y = \sqrt{K_{sp}}$ or $y = \sqrt{(5.0 \times 10^{-13})}$
$= 7.07 \times 10^{-7}$ M
$$\therefore \frac{x}{y} = \frac{6.5 \times 10^{-5}}{7.07 \times 10^{-7}} = 91.63:1$$

Q.19 Determine the solubilities of silver chromate, barium chromate , ferric hydroxide, lead chloride and mercuous iodide at 298 K from their solubility product constant given below. Determine also the molarities of individual ions.

$K_{sp(Ag_2CrO_4)} = 1.1 \times 10^{-12}$
$K_{sp(BaCrO_4)} = 1.2 \times 10^{-10}$
$K_{sp[Fe(OH_3)]} = 1.0 \times 10^{-38}$
$K_{sp[PbCl_2)]} = 1.6 \times 10^{-5}$
$K_{sp[Hg_2I_2]} = 4.5 \times 10^{-29}$

Sol **For Ag_2CrO_4 :**
$K_{sp} = 4S^3$
$$Ag_2CrO_4 \rightleftharpoons 2Ag^+ + CrO_4^{2-}$$
$$S = \sqrt[3]{\frac{K_{sp}}{4}} = \sqrt[3]{\frac{1.1 \times 10^{-12}}{4}} = 6.5 \times 10^{-5}\text{ M}$$
$[Ag^+] = 2 \times 6.5 \times 10^{-5} = 1.30 \times 10^{-4}$ M
$[CrO_4^{-2}] = 6.5 \times 10^{-5}$ M

For $BaCrO_4$:
$K_{sp} = S^2$
$\therefore$ $S = \sqrt{K_{sp}} = \sqrt{1.2 \times 10^{-10}} = 1.1 \times 10^{-5}$ M
$[Ba^{2+}] = 1.1 \times 10^{-5}$ M $= [CrO_4^{2-}]$

For $Fe(OH)_3$:
$K_{sp} = 27\,S^4$

$\therefore \quad S = \sqrt[4]{\dfrac{K_{sp}}{27}} = \sqrt[4]{\dfrac{1.0 \times 10^{-38}}{27}}$

$= 1.39 \times 10^{-10}$ M

$[Fe^{3+}] = 1.39 \times 10^{-10}$ M

$\therefore \quad [OH^-] = 1.39 \times 10^{-10} \times 3 = 4.17 \times 10^{-10}$ M.

For $PbCl_2$:

$K_{sp} = 4\,S^3$

$\therefore \quad S = \sqrt[3]{\dfrac{K_{sp}}{4}} = \sqrt[3]{\dfrac{1.6 \times 10^{-29}}{4}} = 1.59 \times 10^{-2}$ M

$[Pb^{2+}] = 1.59 \times 10^{-2}$ M

$[Cl^-] \;= 2 \times 1.59 \times 10^{-2} = 3.18 \times 10^{-10}$ M

For Hg_2I_2: $\quad Hg_2I_2 \rightleftharpoons Hg_2^{2+} + 2I^-$

$K_{sp} = 4\,S^3$

$\therefore \quad S = \sqrt[3]{\dfrac{K_{sp}}{4}} = \sqrt[3]{\dfrac{4.5 \times 10^{-29}}{4}}$

$= 2.24 \times 10^{-10}$ M

$[Hg_2^{2+}] = 2.24 \times 10^{-10}$ M

$[I^-] = 2 \times 2.24 \times 10^{-10} = 4.48 \times 10^{-10}$ M

Q.20 Calculate the pH of the resultant mixture :

(1) 10 mL of 0.2 M $Ca(OH)_2$ + 25 mL of 0.1 M HCl

(2) 10 mL of 0.01 M H_2SO_4 + 10 mL of 0.01 M $Ca(OH)_2$

(3) 10 ml of 0.1 M H_2SO_4 + 10 mL of 0.1 M KOH

Sol (1) Meq. of $Ca(OH)_2 = 10 \times 0.2 \times 2 = 4$

Meq. of HCl $= 25 \times 0.1 \times 1 = 2.5$

$\therefore$ Meq. of $Ca(OH)_2$ left $= 4 - 2.5 = 1.5$

$\therefore$ N $Ca(OH)_2 = \dfrac{1.5}{10+25} = 4.29 \times 10^{-2}$

$\therefore$ $[OH^-] = 4.29 \times 10^{-2}$ N

$\therefore$ pOH = 1.3675 and pH = 12.6325

(2) Meq. of $H_2SO_4 = 10 \times 0.01 \times 2 = 0.2$

Meq. of $Ca(OH)_2 = 10 \times 0.01 \times 2 = 0.2$

Solution is neutral and pH = 7

(3) Meq. of $H_2SO_4 = 10 \times 0.1 \times 2 = 2$

Meq. of KOH $= 10 \times 0.1 \times 1 = 1$

$\therefore$ Meq. of H_2SO_4 left = 1

$\therefore$ N $H_2SO_4 = 1/20 = 5 \times 10^{-2}$

$\therefore$ $[H^+] = 5 \times 10^{-2}$ N and pH = 1.30

Q.21 The concentration of H^+ ions in 0.10 M solution of a weak acid is 1.0×10^{-5} mol L^{-1}. Calculate the dissociation constant of the acid.

Sol	$HA \rightleftharpoons$	H^+	+ A^-
Initial concentration	0.1	0	0
Equilibrium concentration (mol L^{-1})	$0.1 - 1.0 \times 10^{-5}$	1.0×10^{-5}	1.0×10^{-5}

$$K_a = \frac{[H^+][A^-]}{[HA]} = \frac{1.0 \times 10^{-5} \times 1.0 \times 10^{-5}}{0.10} = 1 \times 10^{-9}$$

Q.22 Determine the concentration of hydroxyl ions in 0.4 M NH_4OH solution having (i) no ammonium chloride, (ii) 5.35 g of NH_4Cl in a litre of the solution. Ionisation constant of NH_4OH is 1.8×10^{-5}.

Sol (i) In absence of NH_4Cl

$[OH^-] = C\alpha = \sqrt{K_b \times C}$

$= \sqrt{1.8 \times 10^{-5} \times 0.4} = 2.68 \times 10^{-3}$ mol L^{-1}

(ii) In presence of NH_4Cl

$[NH_4^+] = \dfrac{5.35}{53.5} = 0.1$ M and $[NH_4OH] = 0.4$M

$$[OH^-] = \frac{K_b[NH_4OH]}{[NH_4^+]}$$

$= \dfrac{1.8 \times 10^{-5} \times 0.4}{0.1} = 7.2 \times 10^{-5}$ mol L^{-1}

Q.23 A solution contains 0.1 M H_2S and 0.3 M HCl. Calculate the concentration of S^{2-} and HS^- ions in solution. Give K_{a1} and K_{a2} for H_2S are 10^{-7} and 1.3×10^{-13} respectively.

Sol $H_2S \rightleftharpoons H^+ + HS^-$

$K_{a1} = \dfrac{[H^+][HS^-]}{[H_2S]}$ …..(1)

$HS^- \rightleftharpoons H^+ + S^{-2}$

$K_{a2} = \dfrac{[H^+][S^{-2}]}{[HS^-]}$ …..(2)

Multiplying both the equation

$K_{a1} \times K_{a2} = \dfrac{[H^+]^2[S^{-2}]}{[H_2S]}$

Due to common ion, the ionization of H_2S is suppressed and the $[H^+]$ in solution is due to the presence of 0.3 HCl.

$[S^{-2}] = \dfrac{K_{a_1} \times K_{a_2}[H_2S]}{[H^+]^2}$

$= \dfrac{1.0 \times 10^{-7} \times 1.3 \times 10^{-13} \times (0.1)}{(0.3)^2} = 1.44 \times 10^{-20}$ M

Put the value of $[S^{-2}]$ in equation (2)

$1.3 \times 10^{-13} = \left(\dfrac{0.3 \times 1.44 \times 10^{-20}}{[HS^-]}\right)$

$[HS^-] = \dfrac{0.3 \times 1.44 \times 10^{-20}}{1.3 \times 10^{-13}} = 3.3 \times 10^{-8}$M

Q.24 The solubility product of $BaSO_4$ is 1.5×10^{-9}. Find out the solubility in (i) pure water and
(ii) 0.1 M $BaCl_2$ solution.

Sol The equilibrium is

(i) $BaSO_4 \rightleftharpoons Ba^{+2} + SO_4^{-2}$

$K_{sp} = [Ba^{+2}]\,[SO_4^{-2}] = S^2$

$1.5 \times 10^{-9} = S^2$

$S = 3.87 \times 10^{-5}$ mol L^{-1}

(ii) Let S' be the solubility of $BaSO_4$ in 0.1M $BaCl_2$ solution

Total Ba^{+2} ions concentration = (S' + C) mol L^{-1}

SO_4^{-2} ion conc. = S' mol L^{-1}

$K_{sp} = (S' + C)\,S' = (S' + 0.1)S'$

$1.5 \times 10^{-9} = S'^2 + 0.1\,S'$

$$S' = \frac{1.5 \times 10^{-9}}{0.1} = 1.5 \times 10^{-8} \text{ mol } L^{-1}$$

Q.25 The solubility of $Mg(OH)_2$ in pure water is 9.57×10^{-3} gL^{-1}. Calculate the solubility in gL^{-1} in gL^{-1} in 0.02 M $Mg(NO_3)_2$ solution.

Sol. Solubility of $Mg(OH)_2$ in pure water

$= 9.57 \times 10^{-3}$ gL^{-1}

$$= \frac{9.57 \times 10^{-3}}{\text{Mol.mass}} \text{ mol } L^{-1} = \frac{9.57 \times 10^{-3}}{58}$$

$= 1.65 \times 10^{-4}$ mol L^{-1}

$$\begin{matrix} Mg(OH)_2 \rightleftharpoons & Mg^{+2} + & 2OH^- \\ & S & 2S \end{matrix}$$

$K_{sp} = [Mg^{+2}]\,[OH^-]^2$

$= S \times (2S)^2 = 4S^3 = 4 \times (1.65 \times 10^{-4})^3$

$= 17.9685 \times 10^{-12}$

S' be solubility of $Mg(OH)_2$ in presence of $Mg(NO_3)_2$

$[Mg^{+2}] = S' + C = S' + 0.02$

$[OH^-] = 2S'$

$K_{sp} = (S' + 0.02)\,(2S')^2$

$17.9685 \times 10^{-12} = 4(S')^2 \,.\, (S' + 0.02)$

$$\frac{17.9685 \times 10^{-12}}{4} = 0.02 \times S'^2$$

$$S'^2 = \frac{4.4921 \times 10^{-12}}{0.02}$$

$S' = 14.9868 \times 10^{-6}$ mol L^{-1}

Solubility of $Mg(OH)_2$ in gL^{-1} = S' × molecular wt.

$= 14.9868 \times 10^{-6} \times 58 = 8.69 \times 10^{-4}$ g L^{-1}

Q.26 A solution has 0.05 M Mg^{2+} and 0.05 M NH_3. Calculate the concentration of NH_4Cl required to prevent the formation of $Mg(OH)_2$ in this solution. K_{sp} of Mg $(OH)_2$ = 9.0×10^{-12} and ionization constant of $NH_3 = 1.8 \times 10^{-5}$.

Sol. The maximum concentration of $[OH^-]$ ions that will precipitate $Mg(OH)_2$ is calculated by applying the equation .

$K_{sp} = [Mg^{+2}]\,[OH^-]^2$

$$[OH^-]^2 = \frac{K_{sp}}{[Mg^{+2}]} = \frac{9.0 \times 10^{-12}}{0.05} = 1.8 \times 10^{-10}$$

$[OH^-] = 1.34 \times 10^{-5}$ M

NH_3 is present in solution in the form of NH_4OH

$$\begin{matrix} NH_3 + H_2O \rightleftharpoons NH_4OH \rightleftharpoons NH_4^+ + OH^- \\ 0.05 \end{matrix}$$

the ionization of NH_4OH is suppressed by the addition of NH_4Cl

$$K_{NH_3} = K_{NH_4OH} = \frac{[NH_4^+]\,[OH^-]}{[NH_4OH]}$$

Whole of the concentration of NH_4^+ ions is provided by NH_4Cl

$$[NH_4^+] = \frac{K_{NH_4OH} \times [NH_4OH]}{[OH^-]} \times \frac{1.8 \times 10^{-5} \times 0.05}{1.34 \times 10^{-5}}$$

i.e. $[NH_4Cl] = 0.067$ M

Q.27 20mL of 0.001 M AgNO solution is added to 1 litre of 0.002 M K_2CrO_4 solution . Will there be any precipitation K_{sp} Ag_2CrO_4 is 2.4×10^{-12}.

Sol. No. of moles of Ag^+ in 20 mL = $\frac{20}{1000} \times 0.001$

$= 2 \times 10^{-5}$

No. of moles CrO_4^{-2} in one litre = 0.002 = 2×10^{-3}

After mixing total volume of the solution

= 1000 + 20 = 1020 ml = 1.02 L

$$[Ag^+] = \frac{2 \times 10^{-5}}{1.02} = 1.96 \times 10^{-5} \text{ M}$$

$$[CrO_4^{-2}] = \frac{2 \times 10^{-3}}{1.02} = 1.96 \times 10^{-3} \text{ M}$$

Ionic Product = $[Ag^+]\;[CrO_4^{-2}] = (1.96 \times 10^{-5})^2 \times (1.96 \times 10^{-3}) = 7.53 \times 10^{-13}$

There will be no precipitation of Ag_2CrO_4 as ionic product is less than solubility product.

Q.28 Calculate the S^{2-} ion concentration in a saturated solution (0.1M) of H_2S whose pH was adjusted to 2 by the addition of HCl. $[K_a = 1.1 \times 10^{-21}]$

Sol $H_2S = \rightleftharpoons 2H^+ + S^{-2}$

$$K_a = \frac{[H^+]^2 S^{-2}}{[H_2S]}$$

$$[S^{-2}] = \frac{K_a[H_2S]}{[H^+]^2}$$

pH = 2 ; So , $[H^+] = 1 \times 10^{-2}$ M

H_2S is a weak electrolyte, So $[H_2S] = 0.1$ M

$$[S^{-2}] = \frac{1.1 \times 10^{-21} \times 0.1}{1 \times 10^{-2} \times 1 \times 10^{-2}} = 1.1 \times 10^{-18}\ M$$

Q.29 K_a for butyric acid is 2×10^{-5}. Calculate pH and hydroxyl ion concentration of 0.2 M aqueous solution of sodium butyrate.

Sol. Sodium butyrate is salt of strong base and weak acid. So

$$[H^+] = \sqrt{\frac{K_w \times K_a}{C}}$$

$$= \sqrt{\frac{10^{-14} \times 2 \times 10^{-5}}{0.2}} = \sqrt{10^{-18}} = 10^{-9}\ M$$

pH = – log [H^+] = – log 10^{-9} = 9

$$[OH^-] = \frac{K_w}{[H^+]} = \frac{10^{-14}}{10^{-9}} = 10^{-5}\ M$$

ANSWER KEY

EXERCISE-1(A)

Q.No.	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20
Ans.	4	2	2	2	1	1	1	1	1	3	2	2	2	2	4	3	4	2	3	1
Q.No.	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36	37	38	39	40
Ans.	1	3	4	3	1	1	2	4	2	3	4	4	4	1	1	1	1	3	4	1
Q.No.	41	42	43	44	45	46	47	48	49	50	51	52	53	54	55	56	57	58	59	60
Ans.	2	4	2	4	4	3	1	1	4	3	3	3	3	3	4	4	2	2	3	3
Q.No.	61	62	63	64	65	66	67	68	69	70	71	72	73	74	75	76	77	78	79	80
Ans.	3	4	3	4	4	2	2	3	4	4	2	4	2	4	3	3	2	1	2	2
Q.No.	81	82	83	84	85	86	87													
Ans.	4	3	3	4	1	4	1													

EXERCISE-1(B)

Q.No.	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20
Ans.	3	2	1	2	1	3	2	2	4	3	3	1	3	4	3	2	3	2	4	3
Q.No.	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36	37	38	39	40
Ans.	4	4	2	2	4	2	2	2	2	1	2	2	2	3	2	3	3	1	4	1
Q.No.	41	42	43	44	45	46	47	48	49	50	51	52	53	54	55	56	57	58	59	60
Ans.	2	4	1	4	3	3	3	3	1	1	1	3	4	3	1	1	2	2	4	3
Q.No.	61	62	63	64	65	66	67	68	69	70	71	72	73	74	75	76	77	78	79	80
Ans.	1	1	2	2	1	3	4	4	1	1	4	3	2	1	2	1	4	4	3	1
Q.No.	81	82	83	84	85	86	87	88	89	90	91	92	93	94	95	96	97	98	99	100
Ans.	1	2	4	4	3	4	2	1	1	2	1	2	4	2	2	4	3	2	1	4
Q.No.	101	102	103	104	105	106	107	108	109	110	111	112	113	114	115	116	117	118	119	120
Ans.	3	3	4	2	2	4	2	1	2	4	1	4	3	2	1	3	3	3	2	2
Q.No.	121	122	123	124	125	126	127	128	129	130	131	132	133	134	135	136	137	138	139	140
Ans.	4	3	3	3	1	3	1	1	4	1	4	1	3	3	1	4	2	1	1	3
Q.No.	141	142																		
Ans.	1	2																		

EXERCISE-2(A)

Q.No.	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20
Ans.	3	1	1	3	4	3	3	1	1	2	3	3	2	4	4	3	2	1	3	1
Q.No.	21	22	23	24	25	26	27	28	29											
Ans.	1	2	2	1	2	2	4	3	1											

EXERCISE-2(B)

Q.No.	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20
Ans.	4	4	4	1	1	3	2	2	3	2	4	3	3	1	1	1	1	2	3	3
Q.No.	21																			
Ans.	1																			

EXERCISE-3(A)

Q.No.	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20
Ans.	3	4	2	2	1	1	4	2	2	3	2	2	1	2	2	2	3	3	4	3
Q.No.	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36	37	38	39	40
Ans.	1	3	4	2	3	2	2	2	1	4	3	1	3	2	4	1	2	3	4	2
Q.No.	41	42	43	44	45	46	47	48	49											
Ans.	1	1	4	4	4	3	2	3	4											

EXERCISE-3(B)

Q.No.	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20
Ans.	2	2	1	1	2	1	2	2	2	2	2	2	2	2	4	3	2	1	1	3
Q.No.	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36	37	38	39	40
Ans.	2	4	4	1	2	1	2	3	2	2	2	2	2	1	3	2	4	4	1	4
Q.No.	41	42	43	44	45	46	47	48	49	50	51	52	53	54	55	56	57	58	59	60
Ans.	4	3	2	1	3	3	4	3	2	1	1	2	4	4	4	4	2	1	2	3
Q.No.	61	62	63	64	65	66	67	68	69	70	71	72	73	74	75	76	77	78	79	80
Ans.	3	4	1	3	1	2	**1**	**1**	**4**	**2**	**2**	**2**	**3**	**1**	**1**	**3**	**2**	**4**	**3**	**4**
Q.No.	81	82	83	84	85	86	87	88	89	90	91	92	93	94	95	96	97	98	99	100
Ans.	1	2	3	1	1	1	2	3	4	3	2	1	4	1	1	3	4	4	4	3
Q.No.	101	102	103	104	105	106	107	108	109	110	111	112	113	114	115	116	117	118	119	120
Ans.	4	4	4	1	4	1	1	1	1	1	4	4	2	3	3	1	2	3	2	3
Q.No.	121	122	123	124	125	126	127	128	129	130	131	132	133	134	135	136	137	138	139	140
Ans.	2	2	2	4	3	3	4	3	1	4	1	1	4	4	3	2	1	3	4	2

EXERCISE-4

Q.No.	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**	**13**	**14**	**15**	**16**	**17**	**18**	**19**	**20**
Ans.	1	3	4	3	2	4	3	3	3	3	4	4	1	4	4	1	3	2	1	3
Q.No.	**21**	**22**	**23**	**24**	**25**	**26**	**27**	**28**	**29**	**30**	**31**	**32**								
Ans.	2	2	1	3	2	1	3	4	2	1	1	3								

Level - 1
IONIC EQUILBRIUM

1. Which one of the following is the best conductor of electricity?
(a) 1M HCl (b) $1MH_2CO_3$ (c) $1MH_3PO_4$ (d) $1MH_2SO_4$

2 For a weak base, the concentration of OH^- at concentration C of base would be (dissociation constant = K_b)
(a) $\sqrt{K_b/C}$ (b) K_b/C (c) $\sqrt{K_b \times C}$ (d) $\sqrt{C/K_b}$.

3 Which one the following is dibasic acid ?
(a) H_3PO_4 (b) H_3PO_3 (c) H_3BO_3 (d) H_3ASO_4.

4. Which one of the following solutions contains the highest concentration of hydronium ion?
(a) 0.1 M HBr (b) 0.1 M HCl (c) 0.1 MHI (d) 0.1 M HF

5. EDTA is a/an
(a) Arrhenius acid (b) Bronsted base
(c) Lewis base (d) All of the above

6. Ionic product of water is 1.0×10^{-14} at $25^\circ C$. This is so
(a) only for water (b) only for acidic solution
(c) only for basic solution (d) for all the three above.

7. pH of a 1000 cc solution is 2. It will not change if
(a) 100 cc of water is added to it
(b) 100 cc of 0.1 M HCl is added to it
(c) 100 cc of N/100 HCl is added to it
(d) 1 cc of 0.1 M HCl is added to it.

8. The pH value of 10^{-3} M aqueous solution of NaCl is
(a) 7 (b) 3 (c) 11 (d) 14

9. The tears coming out of a person's eye have a pH of
(a) 7.0 (b) 7.4 (c) 4.6 (d) 6.4

10. pOH of water is 7.0 at 298 K. If water is heated to 350 K, which of the following would be true?
(a) pOH will decrease (b) pOH will increase
(c) pOH will remain seven
(d) Concentration Of H^+ ions will increase but that of OH^- will decrease.

11. If the solubility of Ag_2CrO_4 is S mole/litre. Its solubility product is
(a) S^2 (b) S^3 (c) $4S^3$ (d) $2S^3$

12. If the solubility of lithium sodium hexafluoroaluminate, $Li_3Na_3(AlF_6)_2$ is 'a' mole/litre, the solubility product is equal to
(a) a^8 (b) $12a^3$ (c) $18a^3$ (d) $2916\ a^8$

13. In which of the following solvents will AgBr have highest solubility ?
(a) 10^{-3} M NaBr (b) 10^{-3} M NH_4OH
(c) Pure water (d) 10^{-3} M HBr.

14. If S_1, S_2, S_3 and S_4 are the solubilities of AgCl in water, in 0.01 M $CaCl_2$ in 0.01 M NaCl and in 0.05 M$AgNO_3$ respectively at a certain temperature, the correct order of solubilites is
(a) $S_1 > S_2 > S_3 > S_4$ (b) $S_1 > S_3 > S_2 > S_4$
(c) $S_1 > S_2 = S_3 > S_4$ (d) $S_1 > S_3 > S_4 > S_4$

15. pH of an acid buffer is given by
(a) $pH = pK_a + \log \frac{[salt]}{[Acid]}$ (b) $pH = pK_a - \log \frac{[salt]}{[Acid]}$
(c) $pH = \frac{1}{2} pK_a + \log \frac{[salt]}{[Acid]}$ (d) $pH = \log K_a + \log \frac{[Acid]}{[salt]}$

16. Which of the following substances on dissolving in water will give a basic solution?
(a) Na_2CO_3 (b) $Al_2(SO_4)_3$ (c) NH_4Cl (d) KNO_3

17. For the salt of weak acid and strong base, the hydrolysis constant is given by the expression
(a) $K_h = \frac{K_w}{K_b}$ (b) $K_a = \frac{K_w}{K_a K_b}$ (c) $K_b = K_a$ (d) $K_h = \frac{K_w}{K_a}$

18. Which of the following relations is correct for degree of hydrolysis of CH_3COONH_4 ?
(a) $h = \sqrt{\frac{k_h}{c}}$ (b) $h = \sqrt{\frac{k_a}{k_b}}$ (c) $h = \sqrt{\frac{K_h}{K_a K_b}}$ (d) $h = \sqrt{\frac{K_a K_b}{K_h}}$

19. During the precipitation of third group of qualitative analysis, ammonium chloride is added before adding ammonium hydroxide. The function of NH_4Cl is to
(a) increase the ionisation of NH_4OH
(b) suppress the ionisation of NH_4OH
(c) convert the ions of group third into their respective chlorides
(d) stabilise the hydroxides of Group III cations

20. Which of the following salts undergoes anionic hydrolysis?
(a) $CuSO_4$ (b) NH_4Cl (c) $FeCl_3$ (d) Na_2CO_3

21. The compound whose 0.1 M solution is basic is
(a) Ammonium acetate (b) Ammonium chloride
(c) Ammonium sulphate (d) Sodium acetate.

22. The precipitate of CaF_2 $\left(K_{sp} = 1.7 \times 10^{-10}\right)$ is obtained when equal volumes of the following are mixed
(a) $10^{-4}\,M\,Ca^{3+} + 10^{-4}\,M\,F^-$ (b) $10^{-2}\,M\,Ca^{2+} + 10^{-3}\,M\,F^-$
(c) $10^{-5}\,M\,Ca^{2+} + 10^{-3}\,M\,F^-$ (d) $10^{-3}\,M\,Ca^{2+} + 10^{-5}\,M\,F^-$

23. What is the decreasing order of strength of the bases OH^-, $NH_2^-, H-C\equiv C^-$ and $CH_3-CH_2^-$?
(a) $CH_3-CH_2^- > NH_2^- > H-C\equiv C^- > OH^-$
(b) $H-C\equiv C^- > CH_3-CH_2^- > NH_2^- > OH^-$
(c) $OH^- > NH_2^- > H-C\equiv C^- > CH_3-CH_2^-$
(d) $NH_2^- > H-C\equiv C^- > OH^- > CH_3-CH_2^-$.

24. In which of the following, the solubility of AgCl will be maximum?
(a) 0.1 M $NaNO_3$ (b) Water (c) 0.1 M NaCl (d) 0.1 M NaBr.

25. The solubility of calcium phosphate in water is x mol L^{-1} at 25^0C. Its solubility product is equal to
(a) $108x^2$ (b) $36x^3$ (c) $36x^5$ (d) $108x^5$

26. The hydrogen ion concentration of 0.2 N CH_3COOH which is 40% dissociated is
(a) 0.08 N (b) 0.12 N (c) 0.80 N (d) 1.2 N

27. The number of H^+ in 1 cc of a solution of pH = 13 is
(a) 6.023×10^7 (b) 1×10^{-13} (c) 6.023×10^{13} (d) 1×10^{16}

28. In decimolar solution, CH_3COOH is ionised to the extent of 1.3%. If log 1.3 = 0.11 , what is the pH of the solution ?
(a) 3.89 (b) 4.89 (c) 2.89 (d) unpredictable

29. Which of the following solution will have pH close to 1.0 ?
(a) 100 ml of M/10HCl+100 ml of M/10NaOH
(b) 55 ml of M/10 HCl + 45 ml of M/10 NaOH
(c) 10 ml of M/10 HCl + 90 ml M/10 NaOH
(d) 75 ml of M/5 HCl + 25 ml of M/5 NaOH.

30. The pK_a of HCN is 9.30.The pH of a solution prepared by mixing 2.5 moles of KCN and 2.5 moles of HCN in water and making up the total volume of 500 ml is
(a) 9.30 (b) 7.30 (c) 10.30 (d) 8.30

31. Solution of 0.1 N NH_4OH and 0.1 N NH_4Cl has pH 9.25. Then pK_b of NH_4OH is
(a) 9.25 (b) 4.75 (c) 3.75 (d) 8.25

32. If the maximum concentration of $PbCl_2$ in water is 0.01 M at 25^0C, its maximum concentration in 0.1 M NaCl will be
(a) $2 \times 10^{-3}M$ (b) $1 \times 10^{-4}M$ (c) $1.6 \times 10^{-2}M$ (d) $4 \times 10^{-4}M$

33. 10 ml of a strong acid solution of pH 2.000 are mixed with 990 ml of a buffer solution of pH=4.000. The pH of the resulting solution will be
(a) 4.100 (b) 4.000 (c) 4.200 (d) 3.800.

34. For the solution of a weak electrolyte AB_2, the degree of dissociation is given by
(a) $\alpha = \sqrt{K_{eq}/2C}$ (b) $\alpha = \sqrt{K_{eq}/C}$
(c) $\alpha = (K/4C)^{1/3}$ (d) $\alpha = (K_{eq}/3C)^{1/3}$

35. Given $K_{a_1}\ K_{a_2}$ for $H_2S = 1.1\times10^{-21} M^3$.
1 L solution of 0.1 M H_2S having $[H^+]$ = 0.1 M contains S^{2-} ions equal to
(a) 6.62×10^3 (b) 6.62×10^4 (c) 6.62×10^5 (d) 6.62×10^6.

Level - 2

More than one option is correct

1. Which of the following mixtures constitute a buffer?
(a) $CH_3COOH + CH_3COONa$ (b) $Na_2CO_3 + NaHCO_3$
(c) NaCl + HCl (d) $NH_4Cl + (NH_4)_2SO_4$

2. Which of the following mixtures constitute a buffer?
(a) $Na_2CO_3 + HCl$ (b) NaOH + CH_3COOH
(c) $NH_3 + CH_3COONH_4$ (d) NaOH + $BaCl_2$

3. In which of the following pairs of solutions is there no effect on the pH upon dilution?
(a) 0.1 M NH_3 and 0.1 M $(NH_4)_2SO_4$
(b) 0.1 M NaH_2PO_4 and 0.1 M Na_2HPO_4
(c) 0.1 M HCl and 0.01 M NaOH
(d) 0.1 M KCl and 0.1 M HCl

4. Which of the following will suppress the ionization of phthalic acid in an aqueous solution?
(a) KCl (b) H_2SO (c) HNO_3 (d) NaOH

5. Which of the following buffers have a pH greater than 7?
(a) $NaHCO_3 + Na_2CO_3$ (b) $CH_3COOH + CH_3COONa$
(c) $Na_3PO_4 + NaH_2PO_4$ (d) $NH_3 + (NH_4)_2SO_4$

6. Which of the following mixtures can act as a buffer?
(a)NaOH+CH_3COONa(1:1 molar ratio)
(b)CH_3COOH+NaOH(2:1 molar ratio)
(c) CH_3COOH+NaOH(3:1 molar ratio)
(d)CH_3COOH+NaOH(1:1 molar ratio)

7. When HCl (g) is passed through a saturated solution of common salt, pure NaCl is precipitated because
(a) HCl is highly soluble in water
(b) The ionic product $[Na^+][Cl^-]$ exceeds its solubility product (K_{sp})
(c) The K_{sp} of NaCl is lowered by the presence of Cl^- ions
(d) HCl causes precipitation

Level – 1
Answer key & Solution

Q.	Ans.	Q.	Ans.	Q.	Ans.	Q.	Ans.
1.	d	11.	c	21.	d	31.	b
2.	a	12.	d	22.	b	32.	d
3.	b	13.	b	23.	a	33.	b
4.	c	14.	b	24.	b	34.	c
5.	d	15.	a	25.	d	35.	a
6.	d	16.	a	26.	a		
7.	c	17.	d	27.	a		
8.	a	18.	c	28.	c		
9.	b	19.	b	29.	d		
10.	a	20.	d	30.	a		

Solution : -

1. 1 M H_2SO_4 produces maximum H^+ ions.

2.
$$\underset{C}{BOH} \rightleftharpoons \underset{0}{B^+} + \underset{0}{OH^-}$$
$$C(1-\alpha) \qquad C\alpha \quad C\alpha$$
$$K_b = \frac{C\alpha . C\alpha}{C(1-\alpha)} = \frac{C\alpha^2}{1-\alpha} = C\alpha^2 \quad \text{or} \quad \alpha = \sqrt{K_b / C}$$
$$[OH^-] = C\alpha \qquad = C\sqrt{K_b / C} = \sqrt{K_b \times C}$$

3. H_3PO_3 contains two ionizable H^+ ions.

4. HI > HBr > HCl > HF.

5. EDTA is Arrhenius acid as it can give H^+ ions in aqueous solutions, a Bronsted base as it can accept protons and Lewis base because N and O in it can donate lone pairs of electrons.

6. Ionic product of water is same for water, neutral, acidic or basic solutions.

7. $\frac{N}{100}$ HCl has also $pH = 2$.

8. NaCl solution is neutral. Its pH = 7.

9. Tears have $pH \simeq 7.4$.

10. On heating H_2O, $[H^+]$ and $[OH^-]$ both increase and remain equal. As $[OH^-]$ increases, pOH decreases.

11. $\underset{S}{Ag_2CrO_4} \rightarrow \underset{2S}{2Ag^+} + \underset{S}{CrO_4^{2-}}$, $K_{sp} = [2S]^2\,[S] = 4S^3$.

12. $\underset{a}{Li_3\,Na_3(AlF_6)_2} \rightarrow \underset{3a}{3Li^+} + \underset{3a}{3\overset{+}{Na}} + \underset{2a}{2AlF_6^{3-}}$

$K_{sp} = (3a)^3(3a)^3(2a)^2 = 2916\,a^8$.

13. AgBr dissolves in NH_4OH to form a soluble complex, $[Ag(NH_3)_2]^+$

14. 0.01 M $CaCl_2 \equiv 0.02$ M Cl^-, 0.01 M NaCl $\equiv 0.01$ M Cl^-,
0.05 M Ag $NO_3 \equiv 0.05$ M Ag^+
$[Ag^+]\,[CL^-] = K_{sp}$ (const.). Hence
$S_2 = K_{sp}/0.02 = 50\,K_{sp}$,
$S_3 = K_{sp}/0.01 = 100\,K_{sp}$
$S_4 = K\,sp/0.05 = 20\,K_{sp}$ $\quad (S_1 = \sqrt{K_{sp}} = \text{maximum})$

15. (a) by Henderson eqn.

16. Na_2CO_3 is a salt of strong base and weak acid.

17. For salt of weak acid and strong base, $K_h = K_w/K_a$.

18. For salt of weak acid and weak base, $h = \sqrt{\frac{K_h}{K_a K_b}}$

19. NH_4Cl is added to NH_4OH to suppress ionization of NH_4OH.

20. Anionic hydrolysis means anion reacting with water
$(Na_2CO_3 + 2H_2O \rightleftharpoons 2NaOH + H_2CO_3$
or $2Na^+ + CO_3^{2-} + 2H_2O \rightleftharpoons 2Na^+ + 2OH^- + H_2CO_3$
or $CO_3^{2-} + 2H_2O \rightleftharpoons 2OH^- + H_2CO_3)$.

21. CH_3COONa is salt of weak acid, CH_3COOH and strong base, NaOH.

22. In (b), after mixing, $[Ca^{2+}][F^-]^2 > K_{sp}$,

23. Their conjugate acids are H-OH, NH_3, $H\text{-}C \equiv C\text{-}H$ and $CH_3 - CH_3$. Their acidic character are $H - OH > CH \equiv CH > NH_3 > CH_3 - CH_3$. A strong acid has a weak conjugate base. Hence the strengths bases will be $CH_3 - CH_2^- > NH_2^- > H - C \equiv C^- > OH^-$.

24. In presence of the given salts, the solubility of Ag Cl decreases.

25. $\underset{x}{Ca_3(PO_4)_2} \rightarrow \underset{3x}{3Ca^{2+}} + \underset{2x}{2PO_4^{3-}}, \; K_{sp} = (3x)^3 \times (2x)^2 = 108x^5$

26. $[H^+] = C\alpha = 0.2 \times 0.40 = 0.08M$

27. pH =13 means $[H^+] = 10^{-13}$ mol L^{-1} or $10^{-13} \times 6.023 \times 10^{23} / 1000 H^+$ ions/cc.
$= 6.023 \times 10^7$

28. $\left[H^+\right] = C\alpha = 0.1 \times 0.013 = 1.3 \times 10^{-3}$
$\therefore \; pH = -\log\left(1.3 \times 10^{-3}\right) = 3 - 0.11 = 2.89.$

29. (a) is exact neutralisation. Hence pH=7
(b) After neutralisation, $\frac{M}{10}$ HCl left = 10ml.
Total volume 100 ml.
Dilution = 10 times $\therefore \; [H^+] = 10^{-2}$ or pH = 2
(c)After neutralistion, $\frac{M}{10}$ NaOH left = 80 ml.
Total volume = 100 ml. pH>7.
(d) After neutralisation, $\frac{M}{5}$ HCl left = 50 ml.
Total volume = 100 ml
Dilution = 2 times

$$\therefore \left[H^+\right] = \frac{1}{10} = 10^{-1}M \text{ or } pH = 1$$

30. As [Salt] = [Acid], pH = pK_a=9.30.

31. As [NH_4Cl] = [NH_4OH], p OH= pK_b or pK_b
= pOH =14 - pH = 14 – 9.25 = 4.75.

32. $\underset{s}{PbCl_2} \rightarrow \underset{s}{Pb^{2+}} + \underset{2s}{2Cl^-}$, $K_{sp} = s(2s)^2 = 4s^3 = 4 \times (10^{-2})^3 = 4 \times 10^{-6}$

In 0.1 M NaCl, [Cl^-]= 0.1 + 2 × 10^{-2}=0.1 M $\left[Pb^{2+}\right]\left[Cl^-\right]^2 = K_{sp}$

or $\left[Pb^{2+}\right](0.10)^2 = 4 \times 10^{-6}$ or $[Pb^{2+}] = 4 \times 10^{-4}M$.

33. pH of buffer remains almost constant.

34. $$\underset{\substack{c \\ c(1-\alpha)}}{AB_2} \rightleftharpoons \underset{\substack{0 \\ c\alpha}}{A^{2+}} + \underset{\substack{0 \\ 2c\alpha}}{2B^-}$$

$$K_{eq} = \frac{c\alpha.(2c\alpha)^2}{c(1-\alpha)} \approx 4C^2\alpha^3 \text{ or } \alpha = (K_{eq}/4c)^{1/3}.$$

35. $H_2S \rightleftharpoons 2H^+ + S^{2-}$.

$$K = 1.1 \times 10^{-21} = \frac{[H^+]^2[S^{2-}]}{[H_2S]} = \frac{[0.1^2][S^{2-}]}{0.1} \text{ or } [S^{2-}] = 1.1 \times 10^{-20}$$

$= 1.1 \times 10^{-20} \times 6.02 \times 10^{23}$ ions

= 6.62×10^3 ions.

Level - 2
Answer key

Q.	Ans.	Q.	Ans.	Q.	Ans.
1.	a, b	2.	a, b	3.	a, b
4.	b, c	5.	a, b	6.	b, c
7.	b, d				

Ionic Equilibrium

SET Self Evaluation Test - 9

1. The most important buffer in the blood consists of **[BHU 1981]**

(a) HCl and $Cl^{\oplus}$
(b) H_2CO_3 and $HCO_3^{\ominus}$
(c) H_2CO_3 and $Cl^{\ominus}$
(d) HCl and $HCO_3^{\ominus}$

2. The solubility product of AgI at $25^{\circ}C$ is $1.0 \times 10^{-16} mol^2 L^{-2}$. The solubility if AgI in $10^{-4} N$ solution of KI at $25^{\circ}C$ is approximately (in mol l^{-1}) **[CBSE PMT 2003]**

(a) 1.0×10^{-8}
(b) 1.0×10^{-16}
(c) 1.0×10^{-12}
(d) 1.0×10^{-10}

3. The pH of the solution: $5\,mL$ of $\frac{M}{5}$, $HCl + 10\,mL$ of $\frac{M}{10}$ $NaOH$ is **[MH CET 2004]**

(a) 5
(b) 3
(c) 7
(d) 8

4. Given that the dissociation constant for H_2O is $K_w = 1 \times 10^{-14} mole^2 / litre^2$. What is the *pH* of a 0.001 *molar KOH* solution **[UPSEAT 2000; MP PET 2001]**

(a) 10^{-11}
(b) 10^{-3}
(c) 3
(d) 11

5. The *p*H of 0.1 *M* solution of the following salts increases in the order **[Pb. CET 2004]**

(a) $NaCl < NH_4Cl < NaCN < HCl$
(b) $HCl < NH_4Cl < NaCl < NaCN$
(c) $NaCN < NH_4Cl < NaCl < HCl$
(d) $HCl < NaCl < NaCN < NH_4Cl$

6. The degree of hydrolysis in hydrolytic equilibrum $A^- + H_2O \rightleftharpoons HA + OH^-$ at salt concentration of 0.001 *M* is $(K_a = 1 \times 10^{-5})$ **[UPSEAT 2004]**

(a) 1×10^{-3}
(b) 1×10^{-4}
(c) 5×10^{-4}
(d) 1×10^{-6}

7. If pK_b for fluoride ion at $25^{o}C$ is 10.83, the ionisation constant of hydrofluoric acid in water at this temperature is **[IIT 1997]**

(a) 1.74×10^{-3}
(b) 3.52×10^{-3}
(c) 6.75×10^{-4}
(d) 5.38×10^{-2}

8. If the hydrogen ion concentration of a given solution is $5.5 \times 10^{-3}\, mol\, litre^{-1}$, the pH of the solution will be **[AMU 1985]**

(a) 2.26
(b) 3.40
(c) 3.75
(d) 2.76

9. Henderson's equation is $pH = pK_a +$ log $\frac{[salt]}{[acid]}$. If the acid gets half neutralized the value of *pH* will be : $[pK_a = 4.30]$ **[RPMT 2000]**

(a) 4.3
(b) 2.15
(c) 8.60
(d) 7

10. The *pH* of a $0.01 M$ solution of acetic acid having degree of dissociation 12.5% is **[JIPMER 2000]**

(a) 5.623
(b) 2.903
(c) 3.723
(d) 4.509

11. Which of the following solutions will have pH close to 1.0 **[IIT 1992; MP PET 1993; AMU 1999]**

(a) $100\,ml$ of $\frac{M}{10} HCl + 100\,ml$ of $\frac{M}{10} NaOH$
(b) $55\,ml$ of $\frac{M}{10} HCl + 45\,ml$ of $\frac{M}{10} NaOH$
(c) $10\,ml$ of $\frac{M}{10} HCl + 90\,ml$ of $\frac{M}{10} NaOH$
(d) $75\,ml$ of $\frac{M}{5} HCl + 25\,ml$ of $\frac{M}{5} NaOH$

12. In which of the following solvents will $AgBr$ have the highest solubility **[CBSE PMT 1992]**

(a) $10^{-3} M\ NaBr$
(b) $10^{-3} M\ NH_4OH$
(c) Pure water
(d) $10^{-3}\ M\ HBr$

13. How many grams of CaC_2O_4 will dissolve in distilled water to make one litre of saturated solution ? (Solubility product of CaC_2O_4 is $2.5\times10^{-9}\ mole^2 litre^{-2}$ and its molecular weight is 128) **[MP PET 1993; MP PMT 2000]**

(a) 0.0064 *gm* (b) 0.0128 *gm*
(c) 0.0032 *gm* (d) 0.0640 *gm*

14. The solubility product of CuS, Ag_2S, HgS are 10^{-31}, 10^{-44}, 10^{-54} respectively. The solubilities of these sulphides are in the order **[CBSE PMT 1997]**

(a) $Ag_2S > CuS > HgS$ (b) $Ag_2S > HgS > Cus$
(c) $HgS > Ag_2S > Cus$ (d) $CuS > Ag_2S > HgS$

15. The solubility product constant K_{sp} of $Mg(OH)_2$ is 9.0×10^{-12}. If a solution is $0.010\,M$ with respect to Mg^{2+} ion, what is the maximum hydroxide ion concentration which could be present without causing the precipitation of $Mg(OH)_2$ **[Pb. PMT 1998]**

(a) $1.5\times10^{-7}\,M$ (b) $3.0\times10^{-7}\,M$
(c) $1.5\times10^{-5}\,M$ (d) $3.0\times10^{-5}\,M$

16. If the K_b value in the hydrolysis reaction $B^+ + H_2O \rightleftarrows BOH + H^+$ is 1.0×10^{-6}, then the hydrolysis constant of the salt would be **[Roorkee Qualifying 1998]**

(a) 1.0×10^{-6} (b) 1.0×10^{-7}
(c) 1.0×10^{-8} (d) 1.0×10^{-9}

17. For a sparingly soluble salt A_pB_q, the relationship of its solubility product (L_S) with its solubility (S) is **[IIT Screening 2001]**

(a) $L_s = S^{p+q}.p^p.q^q$ (b) $L_s = S^{p+q}.p^q.q^p$
(c) $L_s = S^{pq}.p^p.q^q$ (d) $L_s = S^{pq}.(p.q)^{p+q}$

18. Arrange NH_4^+, H_2O, H_3O^+, HF and OH^- in increasing order of acidic nature **[BVP 2003]**

(a) $H_3O^+ < NH_4^+ < HF < OH^- < H_2O$
(b) $NH_4^+ < HF < H_3O^+ < H_2O < OH^-$
(c) $OH^- < H_2O < NH_4^+ < HF < H_3O^+$
(d) $H_3O^+ > HF > H_2O > NH_4^+ > OH^-$

19. How many grams of CaC_2O_4 (molecular weight = 128) on dissolving in distilled water will give a saturated solution $[K_{sp}(CaC_2O_4) = 2.5\times10^{-9}\ mol^2 l^{-2}]$ **[KCET 2003]**

(a) 0.0064 *g* (b) 0.1280 *g*
(c) 0.0128 *g* (d) 1.2800 *g*

20. If the concentration of CrO_4^- ions in a saturated solution of silver chromate is 2×10^{-4}. Solubility product of silver chromate will be **[MP PET 1992; CPMT 1993]**

(a) 4×10^{-8} (b) 8×10^{-12}
(c) 12×10^{-12} (d) 32×10^{-12}

21. According to Bronsted-Lowry concept, the correct order of relative strength of bases follows the order **[Pb. PMT 2001]**

(a) $CH_3COO^- > Cl^- > OH^-$
(b) $CH_3COO^- > OH^- > Cl^-$
(c) $OH^- > CH_3COO^- > Cl^-$
(d) $OH^- > Cl^- > CH_3COO^-$

22. $H_2SO_4^- + OH^- \rightarrow SO_4^{2-} + H_2O$ Which is correct about conjugate acid base pair **[JEE Orissa 2004]**

(a) HSO_4^{2-} is conjugate acid of base SO_4^{2-}
(b) HSO_4^- is conjugate base of acid SO_4^{2-}
(c) SO_4^- is conjugate acid of base HSO_4^-
(d) None of these

23. Which may be added to one litre of water to act as a buffer **[JIPMER 2000]**

(a) One mole of $HC_2H_3O_2$ and 0.5 mole of $NaOH$
(b) One mole of NH_4Cl and one mole of HCl
(c) One mole of NH_4OH and one mole of $NaOH$
(d) One mole of $HC_2H_3O_2$ and one mole of HCl

24. Which of the following base is weakest **[DCE 2003]**

(a) $NH_4OH : K_b = 1.6\times10^{-6}$
(b) $C_6H_5NH_2 : K_b = 3.8\times10^{-10}$
(c) $C_2H_5NH_2 : K_b = 5.6\times10^{-4}$

(d) $C_6H_7N : K_b = 6.3 \times 10^{-10}$

25. $HClO$ is a weak acid. The concentration of H^+ ions in $0.1 M$ solution of $HClO (K_a = 5 \times 10^{-8})$ will be equal to **[CPMT 1993]**

(a) $7.07 \times 10^{-5} m$ (b) $5 \times 10^{-9} m$

(c) $5 \times 10^{-7} m$ (d) $7 \times 10^{-4} m$

26. Upto what *pH* must a solution containing a precipitate of $Cr(OH)_3$ be adjusted so that all of precipitate dissolves

(When $Cr^{3+} = 0.1 mol/l, K_{sp} = 6 \times 10^{-31}$) **[MP PET 2003]**

(a) Upto 4.4 (b) Upto 4.1

(c) Upto 4.2 (d) Upto 4.0

27. NH_4Cl is acidic, because **[JEE Orissa 2004]**

(a) On hydrolysis NH_4Cl gives weak base NH_4OH and strong acid *HCl*

(b) Nitrogen donates a pair of electron

(c) It is a salt of weak acid and strong base

(d) On hydrolysis NH_4Cl gives strong base and weak acid

28. A solution of weak acid *HA* containing 0.01 *moles* of acid *per litre* of solutions has $pH = 4$. The percentage degree of ionisation of the acid and the ionisation constant of acid are respectively **[UPSEAT 2001]**

(a) $1\%, 10^{-6}$ (b) $0.01\%, 10^{-4}$

(c) $1\%, 10^{-4}$ (d) $0.01\%, 10^{-6}$

29. The pH of a buffer solution containg 0.2 *mole per litre* CH_3COONa and 1.5 *mole per litre* CH_3COOH is (*Ka* for acetic acid is 1.8×10^{-5}) **[CPMT 2001]**

(a) 4.87 (b) 5.8

(c) 2.4 (d) 9.2

30. 100 *mL* of $0.04 N HCl$ aqueous solution is mixsed with 100 *mL* of 0.02 *N NaOH* solution. The *p*H of the resulting solution is **[UPSEAT 2004]**

(a) 1.0 (b) 1.7

(c) 2.0 (d) 2.3

31. An alcoholic drink substance $pH = 4.7$ then OH ion concentration of this solution is $(K_w = 10^{-14} mol^2/l^2)$ **[RPMT 2002]**

(a) 3×10^{-10} (b) 5×10^{-10}

(c) 1×10^{-10} (d) 5×10^{-8}

32. In its 0.2 *M* solution, an acid ionises to an extent of 60%. Its hydrogen ion concentration is

(a) 0.6 *M* (b) 0.2 *M*

(c) 0.12 *M* (d) None of these

33. *p*H of 0.1 *M* NH_3 aqueous solution is $(K_b = 1.8 \times 10^{-5})$ **[UPSEAT 2004]**

(a) 11.13 (b) 12.5

(c) 13.42 (d) 11.55

34. 40 *mg* of pure sodium hydroxide is dissolved in 10 litres of distilled water. The *p*H of the solution is **[Kerala PMT 2004]**

(a) 9.0 (b) 10

(c) 11 (d) 12

(e) 8

35. Solubility of PbI_2 is 0.005 *M*. Then, the solubility product of PbI_2 is **[BVP 2004]**

(a) 6.8×10^{-6}

(b) 6.8×10^{6}

(c) 2.2×10^{-9}

(d) None of these

36. A monoprotic acid in a $0.1 M$ solution ionizes to 0.001%. Its ionisation constant is **[MP PET 1985,88,99; MP PMT1988; CPMT 2003]**

(a) 1.0×10^{-3} (b) 1.0×10^{-6}

(c) 1.0×10^{-8} (d) 1.0×10^{-11}

37. Select the pK_a value of the strongest acid from the following **[KCET 2004]**

(a) 1.0 (b) 3.0

(c) 2.0 (d) 4.5

38. At 90°*C*, pure water has H_3O^+ ion concentration of $10^{-6} mol/L^{-1}$. The K_w at 90°*C* is **[DCE 2004]**

(a) 10^{-6} (b) 10^{-14}

(c) 10^{-12} (d) 10^{-8}

39. By adding 20 $ml\ 0.1\ N\ HCl$ to $20\ ml\ 0.1\ N\ KOH$, the pH of the obtained solution will be **[CPMT 1975, 86, 93]**

(a) 0 (b) 7

(c) 2 (d) 9

AS Answers and Solutions

(SET -9)

1. (b) Blood consists of $H_2CO_3 + HCO_3^-$ buffer solution.

2. (c) $AgI \rightleftharpoons \underset{(s)}{Ag^+} + \underset{(s)}{I^-}$; $K_{sp} = S^2 = 10^{-4} \times S$

$$S = \frac{1.0 \times 10^{-16}}{10^{-4}} = 1 \times 10^{-12} \frac{mol^2}{l^2}$$

3. (c) Milliequivalents of $HCl = 5 \times \frac{1}{5} = 1$

Milliequivalents of $NaOH = 10 \times \frac{1}{10} = 1$

$$\therefore\ 5ml \frac{M}{5} HCl = 10ml \frac{M}{5} HCl$$

Hence the solution will be neutral *i.e.*, $pH = 7$.

4. (d) $pH = 14 - pOH = 14 - 3 = 11$

5. (b) HCl is strong acid. In its .1M solution, $[H^+] = 0.1M$ and hence, $pH = 1$

$NH_4Cl_{(aq)}$ hydrolyses in solution and give acidic solution which is less acidic than .1M HCl. $NaCl$ is not hydrolysed in aqueous solutions. Its $pH = 7$ $NaCN$ undergoes hydrolysis in solution to give alkaline solution. So that pH increases in the order, $HCl < NH_4Cl < NaCl < NaCN$

6. (a) $K_h = \frac{K_w}{K_a} = \frac{10^{-14}}{1 \times 10^{-5}} = 10^{-9}$

$K_h = \alpha^2 C$ **;** $\alpha = \sqrt{\frac{K_h}{C}} = \sqrt{\frac{1 \times 10^{-9}}{.001}} = 1 \times 10^{-3}$

7. (c) $K_a \times K_b = K_w$

$$\therefore K_a = \frac{K_w}{K_b} = \frac{10^{-14}}{1.48 \times 10^{-11}} = 6.75 \times 10^{-4}$$

8. (a) $[H^+] = 5.5 \times 10^{-3}$ *mole/litre*

$pH = -\log[H^+]$; $pH = -\log[5.5 \times 10^{-3}]$; $pH = 2.26$

9. (a) $pH = pK_a + \log\frac{[\text{Salt}]}{[\text{Acid}]}$

$$pH = 4.3 + \log\frac{\frac{1}{2}}{\frac{1}{2}} = 4.3 + \log 1;$$

$pH = 4.3 + 0 = 4.3$

10. (b) $[H^+] = C\alpha = 0.01 \times \frac{1.25}{100}$

$H^{+} = 1.25 \times 10^{-3}$;

$pH = \text{between} 2 \text{ or } 3 = 2.90$

11. (d) M.eq. of $HCl = \frac{1}{5} \times 75 = 15$

M.eq. of $NaOH = 25 \times \frac{1}{5} = 5$

Total No. of eq. $= 15 - 5 = 10$

Total volume = 100

Normality $= \frac{10}{100} = \frac{1}{10}, [H^{+}] = 10^{-1} M$

12. (b) *AgBr* are not dissolved in *NaBr* and *HBr* due to common ion effect. And pure water is a neutral solvent. They do not have ions.

13. (a) CaC_2O_4 is a binary electrolyte. Then solubility is

$S = \sqrt{K_{sp}} = \sqrt{2.5 \times 10^{-9}}$

$= 5 \times 10^{-5}$ *mole/l.* $= 0.0064$ *gm/l.*

14. (a)

15. (d) $\underset{K_{sp}}{Mg(OH)_2} \rightleftharpoons \underset{S}{Mg^{++}} + \underset{(2S)^2}{2OH^{-}}$

$K_{sp} = S \times 4S^2$

$\frac{K_{sp}}{S \times 4} = S^2 = \frac{9 \times 10^{-12}}{.010 \times 4} = 2.25 \times 10^{-10}$

$S = \sqrt{2.25 \times 10^{-10}} = 1.5 \times 10^{-5}$ *m/l*

16. (c) For hydrolysis of B^{+}; $K_H = \frac{K_w}{K_b}$

$= \frac{10^{-14}}{10^{-6}} = 10^{-8}$.

17. (a) $A_pB_q \rightleftharpoons pA^{1+} + qB^{p-}$

$L_s = [A^{q+}]^p [B^{p-}]^q = (p \times S)^p (q \times S)^q = S^{p+q}.p^p.c$

.

18. (c) $H_3O^{+} > HF > NH_4^{+} > H_2O > OH^{-}$.

Acidic nature is decreasing order.

19. (a) Solubility of $CaC_2O_4 = \sqrt{K_{sp}} = \sqrt{2.5 \times 10^{-9}}$

$= 5 \times 10^{-5} mol L^{-1}$

$= 5 \times 10^{-5} \times 128 = 640 \times 10^{-5} = 0.0064 g$

20. (d) K_{sp} of $Ag_2CrO_4 = [Ag^{+}]^2 [Cro_4^{--}]$

$CrO_4^{--} = 2 \times 10^{-4}$ then $Ag^{+} = 2 \times 2 \times 10^{-4}$

$K_{sp} = (4 \times 10^{-4})^2 (2 \times 10^{-4}) = 32 \times 10^{-12}$

21. (c) Relative strength of bases can be shown by their conjugated acids.

Conjugate acid of OH^{-} is H_2O which is a weak acid conjugate acid of CH_3COO^{-} is CH_3COOH which is stronger than H_2O. while conjugate acid of Cl^{-} is HCl which is strongest out of there. so the order of relative strength of bases is $OH^{-} > CH_3COO^{-} > Cl^{-}$.

22. (a) $\underset{\text{Conjugate acid}}{HSO_4^{-}} + OH^{-} \rightarrow \underset{\text{Conjugate base}}{SO_4^{2-}} + H_2O$

23. (a) One mole oxalic acid & 0.5 mole of $NaOH$ will make.

24. (b) Smallest value of K_b indicates that aniline $(C_2H_5NH_2)$ is the weakest base.

25. (a) $[H^{+}]^2 = C.\alpha = 0.1 \times 5 \times 10^{-8}$

$H^{+} = \sqrt{5 \times 10^{-9}} = 7.07 \times 10^{-5} M.$

26. (d) $K_{sp} = [Cr^{3+}][OH^{-}]^3$

$[OH]^{-3} = K_{sp/Cr^{3+}} = \frac{6 \times 10^{31}}{1 \times 10^{-1}} = 6 \times 10^{-30}$

$[OH]^{-} = 1.8 \times 10^{-10}$

$pOH = (\log 1.8 + \log 10^{10}) = 10 + 0.25 + 1$

$= 11.25$

$pH = 14 - 11.25 = 2.27$

27. (a) $NH_3Cl + H_2O \rightleftharpoons NH_4OH + HCl$

NH_4Cl is a salt of weak base & strong acid so solution will be acidic.

28. (a) $H^{+} = C\alpha$

$\alpha = \frac{H^{+}}{C} = \frac{10^{-4}}{10^{-2}} = 10^{-6}$

29. (a) $pH = -\log K_a + \log \frac{[\text{Salt}]}{[\text{Acid}]}$

$= -\log [1.8 \times 10^{-5}] + \log \frac{0.2}{0.1} = 4.87$

30. (c) $N_1V_1 = .04 \times 100 = 4$

$N_2V_2 = .02 \times 100 = 2$

$N_1V_1 - N_2V_2 = N_3V_3$

$4 - 2 = N_3 \times 200, N_3 = 10^{-2} M$

$pH = \log 10 \frac{1}{H^{+}} = \log 10 \frac{1}{10^{-2}} = 2.$

31. (b) $pH = 4.7$

$$pH + pOH = 14;\ pH = 14 - 4.7;\ pOH = 9.3$$

$$[OH^-] = \text{Antilog}\ [-pOH] = \text{Antilog}[-9.3]$$

$$[OH^-] = 5 \times 10^{-10}$$

***

32. (c) $[H^+] = C.\alpha, \ = 0.2 \times 0.60 = 0.12M$

33. (a) $NH_4OH \rightleftharpoons NH_4^+ + OH^-$

$$K_b = C\alpha^2;\ \frac{1.8\times10^{-5}}{.1} = \alpha^2;\ \alpha = 1.34\times10^{-3}$$

$$[OH^-] = \alpha\ .\ C = 1.34\times10^{-3}\times.1$$

$$pOH = \log10\frac{1}{1.34\times10^{-4}};\ pOH = 2.87$$

$$pH + pOH = 14;\ pH + 2.87 = 14$$

$$pH = 14 - 2.87;\ pH = 11.13$$

34. (b) $M = \dfrac{\text{Solute in 1 litre solution}}{\text{Molecular weight of solute}}$

$$= \frac{40\times10^{-3}}{40}\times\frac{1}{10} = 10^{-4}M$$

$$pOH = \log10\frac{1}{[OH^-]} = \log10\frac{1}{10^{-4}} = 4$$

$$pH + pOH = 14;\ pH + 4 = 14 \Rightarrow pH = 10.$$

35. (d) $\underset{x}{PbI_2} \rightarrow \underset{\ }{Pb} + \underset{2x}{I_2}$

$$K_{sp} = 4x^3 = 4(.005)^3$$

$$= 4\times.005\times.005 = .4\times10^{-6}.$$

36. (d) $\therefore$ Monoprotic acid HA

$HA \rightleftharpoons H^+ + A^-$

Ionisation constant = ?

$$\alpha = 0.001\% = \frac{0.001}{100} = 10^{-5}$$

$$K = \frac{\alpha^2}{V} = \frac{[10^{-5}]^2}{10} = 10^{-11}.$$

37. (a) $pKa <<$ then strongest acid

$pKa >>$ then weak acid

$$pKa \propto \frac{1}{\text{Acidic strengt}}$$

38. (c) $\underset{10^{-6}}{H_3O^+} \rightarrow \underset{10^{-6}}{H_2O} + \underset{10^{-6}}{H^+}$

$$K_w = [H_2O][H^+] = [10^{-6}][10^{-6}] = 10^{-12}$$

39. (b) Neutralization reaction will takes place and form salt of strong acid and strong base. Which does not hydrolysed and thus $pH = 7$.

Chemical Kinetics

Rate of Reaction

Rate of a reaction is defined as the increase in molar concentration of a product per unit time or decrease in molar concentration of a reactant per unit time. Molar concentration is normally measured in moles per litre, the rate of a reaction is specified in mole per litre per time.

Average and Instantaneous Rate: The quantity $\frac{\Delta x}{\Delta t}$ is known as average rate, where Δx is the change in concentration in Δt time. As we have discussed in chemical equilibrium rate of change of concentration of reactant decreases as the reaction proceeds. This means that rate of change of concentration is not constant. If the time interval is quite large then average rate will show large deviations from the actual rate.

Instantaneous Rate: In order to precisely define rate time interval Δt is made smaller

i.e. instantaneous rate = average rate as Δt approaches zero.

$$= \underset{\Delta t \to 0}{}\left[\frac{\Delta[A]}{\Delta t}\right] = \frac{d[A]}{dt}$$

Consider the hypothetical reaction

$$A + 2B \longrightarrow 3C + D$$

Rate of disappearance of A = $-\frac{d[A]}{dt}$

Rate of disappearance of B = $-\frac{d[B]}{dt}$

Rate of appearance of C = $+\frac{d[C]}{dt}$

Rate of appearance of D = $+\frac{d[D]}{dt}$

But from the stoichiometry it is apparent that when one mole of A is reacted, two moles of B are also consumed.

i.e. rate of disappearance of B = 2 × rate of disappearance of A

$$-\frac{d[B]}{dt} = 2 \times -\frac{d[A]}{dt} \text{ or } -\frac{d[A]}{dt} = \frac{1}{2} - \frac{d[B]}{dt}$$

Similarly we can prove that

$$-\frac{d[A]}{dt} = \frac{1}{3} + \frac{d[C]}{dt}$$

So, rate of reaction = $-\frac{d[A]}{dt} = -\frac{1}{2}\frac{d[B]}{dt} = \frac{1}{3}\frac{d[C]}{dt} = \frac{d[D]}{dt}$

We can also generalize our statement i.e. for a general reaction

$$m_1A + m_2B \longrightarrow n_1C + n_2D$$

Rate of reaction = $\frac{1}{m_1} - \frac{d[A]}{dt} = \frac{1}{m_2} - \frac{d[B]}{dt} = \frac{1}{n_1} + \frac{d[C]}{dt} = \frac{1}{n_2} + \frac{d[D]}{dt}$

Illustration 1: ***The rate law of a chemical reaction given below :***

$2NO + O_2 \longrightarrow 2NO_2$

is given as rate = $K[NO]^2 [O_2]$. How will the rate of reaction change if the volume of reaction vessel is reduced to 1/4th of its original value ?

Solution: For, $2NO + O_2 \longrightarrow 2NO_2$

$Rate = K[NO]^2 [O_2]$

Let a mole of NO and b mole of O_2 be taken to start a reaction at any time in a vessel of V litre.

$$r = K\left[\frac{a}{V}\right]^2\left[\frac{b}{V}\right] \qquad \text{......(1)}$$

If volume of vessel is reduced to V/4, then for same mole of NO and O_2

$$r_2 = K\left[\frac{a}{V/4}\right]^2\left[\frac{b}{V/4}\right]$$

$$= 64K\left[\frac{a}{V}\right]^2\left[\frac{b}{V}\right] \qquad \text{....(2)}$$

By eqs. (1) and (2),

$$\therefore \quad \frac{r_2}{r_1} = 64$$

or r_2 *is 64 times of* r_1.

Factors Affecting the Reaction Rate

The rate of any particular reaction depends upon the following factors:

1. ***Concentration of the reactants:*** Greater the concentrations of the reactants, faster is the reaction. Conversely, as the concentrations of the reactants decrease, the rate of reactions also decreases.
2. ***Temperature:*** The rate of reaction increases with increase of temperature. In most of the cases, the rate of reaction becomes nearly double for 10 K rise of temperature. In some cases, reactions do not take place at room temperature but take place at higher temperature.

3. **Presence of Catalyst:** A catalyst generally increases the speed of a reaction without itself being assumed in the reaction. In case of reversible reactions, a catalyst helps to attain the equilibrium quickly without disturbing the state of equilibrium.

4. **Surface area of the reactants:** For a reaction involving a solid reactant or catalyst, the smaller is the particle size, i.e., greater is the surface area, the faster is the reaction.

5. **Presence of light:** Some reactions do not take place in the dark but take place in the presence of light e.g., $H_2 + Cl_2 \rightarrow 2HCl$. Such reactions are called “photochemical reactions”.

Now we shall discuss the quantitative effect of concentration and temperature on the rate of reaction. the study of quantitative effect of concentration on the rate of reaction leads to the introduction of a number of new terms such as order of reaction, specific reaction rate (rate constant) and molecularity of reaction. It also leads to the study of mechanism of the reactions. These different aspects are discussed in the following sections.

Molecularity and Order

Single step reaction is called *elementary* reaction while a reaction occurring in two or more steps is called *complicated* or *consecutive* reaction. Each step of a complicated reaction is an elementary reaction.

The minimum number of molecules, atoms or ions of reactants required for an elementary reaction to occur is indicated by the sum of the stoichiometric coefficients of the reactant(s) in the chemical equation, is known molecularity of the reaction. Thus for an elementary reaction represented by the general chemical equation.

$aA + bB \longrightarrow \text{products}$
molecularity = a + b

Examples:	Reactions	Molecularity
	$PCl_5 \rightleftharpoons PCl_3 + Cl_2$	1
	$H_2 + I_2 \rightleftharpoons 2HI$	2

A complicated reaction has no molecularity of its own but molecularity of each of the steps involved in its mechanism.

For example:

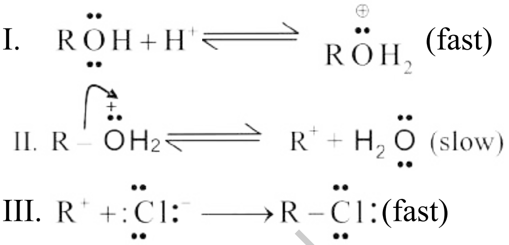
The reaction: $2NO + 2H_2 \rightleftharpoons N_2 + 2H_2O$, takes place in the sequence of following three steps.

I. $NO + NO \rightleftharpoons N_2O_2$ (fast and reversible)
II. $N_2O_2 + H_2 \longrightarrow N_2O + H_2O$ (slow)
III. $N_2O + H_2 \longrightarrow N_2 + H_2O$ (fast)

The molecularity of each step involved in mechanism is 2 i.e., each step is bimolecular. So as regards the molecularity of the reaction under consideration we simply say that the reaction has mechanism and each step involved in it is bimolecular

However, there is another view also - according to which molecularity of a complicated reaction is taken to be equal to the number of molecules, atoms or ions of reactant(s) and/or intermediates coming into contact and colliding simultaneously in the slowest step i.e. the rate-determining step of the reaction.

For example the reaction ROH + HCl $\xrightarrow{ZnCl_2}$ RCl + H_2O, which actually is a nucleophilic substitution reaction



Here the step II is the slowest step and hence the r.d.s. the molecularity of which is one. Therefore, the mechanism is called substitution nucleophilic unimolecular (S_N1) and the reaction is said to follow S_N1 mechanism.

The mathematical equation showing the relation of rate of reaction with concentration of reactant(s) is called rate-law of the reaction. For example, the kinetic experiment carried on the reaction.

$$2NO + 2H_2(g) \longrightarrow N_2(g) + 2H_2O\ (g)$$

has shown that (i) rate increases 4 - fold when conc. of NO is doubled keeping the conc. of H_2 constant (ii) rate gets just doubled when conc. of H_2 is doubled keeping that of NO constant, and (iii) rate increases 8 - fold when concentrations of both NO and H_2 are doubled simultaneously. These experimental rate data fit into following equation.

$$\text{Rate } \alpha\ [NO]^2[H_2]$$

This equation is called experimentally observed "Rate law" of the reaction.

Order of reaction is defined as the sum of the powers of the concentration terms appearing in experimentally observed rate law. Thus for the reaction (reduction of nitric oxide by hydrogen) considered above.

Order w.r.t. NO = 2
Order w.r.t. H_2 = 1
Overall order = 2+ 1 = 3

In general, let a reaction represented by the chemical equation:

$$aA + bB \longrightarrow \text{Products}$$

obeys the following rate law.

$$\text{Rate } \alpha\ [A]^m\ [B]^n, \text{ or Rate } = k[A]^m\ [B]^n$$

Where k = rate constant of reaction, a constant at constant temp and is actually the rate of reaction when conc. of each reactant is equal to unity k is also called velocity coefficient or specific reaction rate.

Note that m and n are experimental quantities which may or may not be equal to the respective stoichiometric coefficients.

Also note that if either of A or B is taken in large excess as compared to another, the order w.r.t this reactant will be zero so order = m (when B is in large excess), and order = n (when A is large excess),i.e.,

Rate = $k'[A]^m$, $k' = k[B]^n$ another constant, when B is in large excess.

Order w.r.t. A = m
Order w.r.t. B = 0

Rate = $k''[B]^n$, $k'' = k[A]^m$ = another constant, when A is in large excess.

Order w.r.t. A = 0
Order w.r.t. B = n

k′ or k″ is actually known as pseudo rate constant

Thus, a bimolecular reaction conforms to the first - order when one of the reactants is taken in large excess and the reaction is said to be pseudo unimolecular or pseudo first order. An example of this is the hydrolysis of ester by dil. acid i.e.

$$CH_3COOC_2H_5 + H_2O^+ \xrightarrow{H^+} CH_3COOH + C_2H_5OH$$

The reactions is originally of second - order obeying the kinetics.

$$\text{Rate} = k\,[CH_3COOC_2H_5]\,[H_2O]$$

But the reaction is usually carried out taking dilute aqueous solution of ester and acid (HCl) such that in the reaction mixture water exists in large excess as compared to ester or better to say, water has almost its maximum concentration of 55.5 mole L^{-1}. So there is no appreciable change in the concentration of water and the same remains practically constant. $k[H_2O]$ becomes another constant (k′) called pseudo rate constant and reactions obeys the following 1st order kinetics

$$\text{Rate} = k'\,[CH_3COOC_2H_5]$$

Thus, the molecularity of the above reaction is 'two' but its order is 'one;.

In the light of the above concept one may define order of reaction as " the number of molecules of the reactant(s) whose concentration alters during the chemical change is the order of reaction".

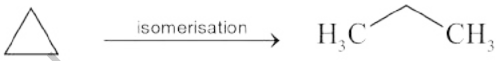
Distinction between Molecularity and Order

i) Molecularity is a theoretical property while order is an experimental property.

ii) Molecularity concerns to mechanism, order concerns to kinetics

iii) Molecularity is always a whole number and never zero while order may be any number zero, fractional and integral.

iv) Molecularity is invariant but order may vary with change in experimental condition. As for example, the isomerisation of cyclo - propane represented by the chemical equation given below is a first order reaction at high cyclo propane pressure and is a second order reaction at low cyclo propane pressure.



v) Reactions of higher molecularity is rare since the chance of coming into contact and colliding simultaneously decreases as the number of molecules involved in collision increases.

Unit of rate constant

$nA \longrightarrow$ Product

$$\frac{dx}{dt} = k[\text{conc.}]^n$$

$$\frac{[\text{conc.}]}{\text{sec}} = k[\text{conc.}]^n$$

$\mathbf{k = [conc.]^{1-n} sec^{-1}}$ $= [\text{mole/litre}]\text{sec}^{-1}$

Illustration 2: ***Dinitrogen pentaoxide decomposes as follows :***

$$N_2O_5 \longrightarrow 2NO_2 + \frac{1}{2}O_2.$$

If, $\frac{-d[N_2O_5]}{dt} = K_1[N_2O_5]$; $\frac{d[NO_2]}{dt} = K_2[N_2O_5]$; $\frac{d[O_2]}{dt} = K_3[N_2O_5]$

Derive a relation between K_1, K_2 and K_3.

Solution: For the given change

$$\frac{-d[N_2O_5]}{dt} = +\frac{1}{2}\frac{d[NO_2]}{dt} = 2\frac{d[O_2]}{dt}$$

On substituting values as given,

$$K_1[N_2O_5] = \frac{1}{2}K_2[N_2O_5] = 2K_3[N_2O_5]$$

or $2K_1 + K_2 = 4K_3$

Illustration 3: ***From the following data for the reaction between A and B, calculate the order of the reaction with respect to A and with respect to B.***

[A]/mol L^{-1}	***[B]/mol L^{-1}***	***Initial rate/mole L^{-1} s^{-1}***

2.5×10^{-4}	***3.0×10^{-5}***	***5.0×10^{-4}***
5.0×10^{-4}	***6.0×10^{-5}***	***4.0×10^{-3}***
1.0×10^{-3}	***6.0×10^{-5}***	***1.6×10^{-2}***

Solution: Let the order with respect to A be a and with respect to B be b. The rate law would then be represented as

Rate = $k\,[A]^a\,[B]^b$

Therefore

$5.0 \times 10^{-4} = k[2.5 \times 10^{-4}]^a\,[3.0 \times 10^{-5}]^b$ . . . . . .(i)

Using second data, gives

$4.0 \times 10^{-3} = k[5.0 \times 10^{-4}]^a[6.0 \times 10^{-5}]^b$ . . . . .(ii)

and using third data, gives

$1.6 \times 10^{-2} = k[1.0 \times 10^{-3}]^a\,[6.0 \times 10^{-5}]^b$ . . . . .(iii)

Dividing equation (i) by (ii),

$$\frac{4.0\times10^{-3}}{5.0\times10^{-4}} = \frac{k[5.0\times10^{-4}]^a[6.0\times10^{-5}]^b}{k[2.5\times10^{-4}]^a[3.0\times10^{-5}]^b}$$

$8 = (2)^{a+b}$

$2^3 = 2^{a+b}$

$\therefore\ a + b = 3$

Similarly, dividing equation (iii) by (ii),

$$\frac{4.0\times10^{-3}}{1.6\times10^{-2}} = \frac{k[5.0\times10^{-4}]^a[6.0\times10^{-5}]^b}{k[1.0\times10^{-3}]^a[6.0\times10^{-5}]^b}$$

$$\frac{1}{4} = \left(\frac{1}{2}\right)^a$$

or $4 = 2^2 = 2^a$

so, order with respect to A is two and with respect to B is one.

Rate Law and Mechanism

As already mentioned in the reaction:

$$2NO + 2H_2 \longrightarrow N_2 + 2H_2O$$

Obeys the following third order kinetics

$$\text{Rate} \propto [NO]^2\,[H_2]$$

The kinetics is not in tune with chemical equation. As the law of mass action suggests each concentration term should be raised to power 2. Neither experimental facts nor those coming from Law of mass action can be unacceptable to us. Under this condition we are led to believe that the reaction does not occur according to the chemical equation as written. That is the reaction is not elementary but is complicated. In order to explain the observed rate law following mechanism has been proposed.

I $NO + NO \rightleftharpoons N_2O_2$ (fast and reversible)
II $N_2O_2 + H_2 \longrightarrow N_2O + H_2O$ (slow)

III $N_2O + H_2 \longrightarrow N_2 + H_2O$ (fast)

The step II being the slowest i.e., the rate - determining step (r.d.s.). Note that the rate of formation of N_2 cannot be faster than the rate of formation of N_2O. So, the rate of overall reaction or rate of formation of N_2 will be equal to the rate of step II which according to law of mass action may be given as.

Rate of overall reaction = Rate of step II = $k[N_2O_2]\,[H_2]$

Where k = rate constant of step II

The conc. of the intermediate (N_2O_2) may be evaluated by applying law of mass action upon the equilibrium existing in step I as mentioned below.

$$K_c = \frac{[N_2O_2]}{[NO]^2} \quad \text{or} \quad [N_2O_2] = K_c\,[NO]^2$$

Putting this in the rate expression, we get

$$\text{Rate} = k.k_c[NO]^2[H_2] = k_{obs}\,[NO]^2[H_2]$$

Where $k_{obs} = k.k_c$ = observed rate constant of the reaction

$$\text{Rate}\ \alpha\ [NO]^2\,[H_2]$$

This is the same rate - law as observed experimentally.

Illustration 4: ***The possible mechanism for the reaction***

$2\,NO + Br_2 \longrightarrow 2\,NOBr$

is $NO + Br_2 \longrightarrow NOBr_2$ (fast);

$NOBr_2 + NO \longrightarrow 2\,NOBr$ (slow).

Establish the rate law.

Solution: As the slowest step is the rate determining step, therefore the rate law is

$R = k[NOBr_2]\,[NO]$

Now since $NOBr_2$ is an intermediate its concentration can be calculated from step 1 as follows:

$$K = \frac{[NOBr_2]}{[NO][Br_2]} \qquad [K = \text{eq. constant}]$$

or $[NOBr_2] = K\,[NO]\,[Br_2]$

Substituting this value in above equation

$r = k.\,K[NO]^2[Br_2]$

or rate $= k'\,[NO]^2\,[Br_2]$ $[\because\ k\cdot K = \text{constant } k']$

$\therefore$ Rate $= k'\,[NO]^2\,[Br_2]$

Reactions of the First Order

A reaction is said to be of the first order if the rate of the reaction depends upon one concentration term only. Thus we may have

For the reaction : $A \rightarrow$ Products
Rate of reaction $\propto [A]$.

For the reaction : $2A \rightarrow$ Products
Rate of reaction $\propto [A]$ only.

For the reaction : $A + B \rightarrow$ Products
Rate of reaction $\propto [A]$ or $[B]$ only.

Let us consider the simplest case viz.

$$A \rightarrow \text{Products}$$

Suppose we start with ‘a’ moles per litre of the reactant A. After time t, suppose x moles per litre of it, have decomposed. Therefore, the concentration of A after time t = (a – x) moles per litre. Then according to Law of Mass Action.

Rate of reaction $\propto (a - x)$

i.e., $$\frac{dx}{dt} \propto (a - x) \text{ or } \frac{dx}{dt} = k(a - x) \quad \ldots (1)$$

where k is called the rate constant or the specific reaction rate for the reaction of the first order. The expression for the rate constant k may be derived as follows :

Equation (1) may be rewritten in the form

$$\frac{dx}{a - x} = kdt \quad \ldots(2)$$

Integrating equation (2), we get $\int \frac{dx}{a - x} = \int kdt$

or $$k = \frac{1}{t} \ln \frac{a}{a - x} \quad \ldots(3)$$

or $$k = \frac{2.303}{t} \log \frac{a}{a - x} \quad \ldots(4)$$

Equation (4) is sometimes written in another form which is obtained as follows :

If the initial concentration is $[A]_0$ and the concentration after time t is $[A]$, then putting $a = [A]_0$ and $(a - x) = [A]$ equation (iv) becomes

$$k = \frac{2.303}{t} \log \frac{[A]_0}{[A]} \quad \ldots (5)$$

Further, putting a = $[A]_0$ and (a – x) = [A] in eqn. (3), we get

$$kt = \ln \frac{[A]_0}{[A]}$$

which can be written in the exponential form as

$$\frac{[A]_0}{[A]} = e^{kt} \text{ or } \frac{[A]}{[A]_0} = e^{-kt} \text{ or } [A] = [A]_0\, e^{-kt} \qquad \ldots (6)$$

Illustration 5: ***What will be the initial rate of a reaction if its rate constant is 10^{-3} min^{-1} and the concentration of reactant is 0.2 mol dm^{-3} ? How much of reactant will be converted into products in 200 minute ?***

Solution: Since K has unit min^{-1} and thus, given reaction is of I order

Now Rate = $K[\ ]^1$

Rate = $10^{-3} \times [0.2]^1 = 2 \times 10^{-4}$ mol dm^{-3} min^{-1}

Also $$K = \frac{2.303}{t}\log_{10}\frac{a}{(a-x)}$$

$$\therefore \quad 10^{-3} = \frac{2.303}{200}\log_{10}\frac{100}{(100-x)}$$

$$\therefore \quad x = 18.12\%$$

Illustration 6: ***The half time of first order decomposition of nitramide is 2.1 hour at 15°C.***

$NH_2NO_2(s) \longrightarrow N_2O(g) + H_2O(l)$

If 6.2 g of NH_2NO_2 is allowed to decompose, calculate

a) time taken for NH_2NO_2 to decompose 99% and

b) volume of dry N_2O produced at this point measured at STP.

Solution: For a first-order reaction, rate constant expression is $k = \frac{2.303}{t}\log\frac{[A]_0}{[A]_t}$

Initial moles of nitramide = $\frac{6.2}{62} = 0.1$

$$\therefore \quad t = \frac{2.303 \times 2.1}{0.693}\log\frac{0.1}{0.001} = 13.95 \text{ hours}$$

Since, the decomposition is 99%, so 99% of the initial moles of NH_2NO_2 would be converted to N_2O.

Moles of N_2O = $\frac{0.1 \times 99}{100}$

$\therefore$ Volume of N_2O at STP = $\frac{0.1 \times 99 \times 22.4}{100} = 2.217$ litre.

Some Important Characteristics of First Order Reactions

i) Any reaction of the first order must obey equation (5) or (6). This may be tested in any one of the following ways :

a) ***Substitution method:*** Starting with a known concentration `a' or $[A]_0$, the concentration of the reactant (a – x) or [A] at different intervals of time may be noted. For every value of t, the corresponding value of (a – x) i.e. [A] may be substituted in equation (vi) or (vii). If the values of k thus obtained are nearly constant (within the experimental error), the reaction is of the first order.

b) ***Graphical method:*** Equation (6) may be written as

$$\frac{k}{2.303}t = \log\frac{[A]_0}{[A]} = \log[A]_0 - \log[A]$$

or $$\log[A] = -\frac{k}{2.303}t + \log[A]_0 \qquad \text{... (7)}$$

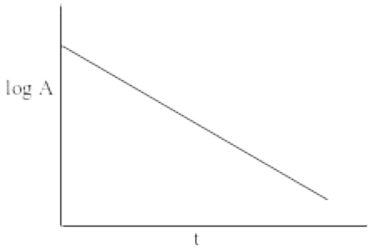
This is the equation of a straight line (y = mx + c). Thus if log (A] or log (a – x) values are plotted against time `t', the graph obtained should be a straight line if the reaction is of the first order.

The intercept made on the y-axis would be `log $[A]_0$'

and the slope of the line would be equal to $\left(-\frac{k}{2.303}\right)$

i.e.,slope = $-\frac{k}{2.303}$

From this, the value of k can be calculated.



ii) ***Half-life Period:*** The time taken for any fraction of the reaction to be completed is independent of the initial concentration. For example, let us test the truth of this statement for half of the reaction to be completed. Equation (5) may be written as

$$t = \frac{2.303}{k}\log\frac{a}{a-x} \qquad \text{... (8)}$$

When half of the reaction is completed, x = a/2. Representing the time taken for half of the reaction to be completed by $t_{1/2}$ equation (8) becomes

$$t_{1/2} = \frac{2.303}{k}\log\frac{a}{a-\frac{a}{2}} = \frac{2.303}{k}\log 2 = \frac{0.693}{k}$$

i.e, $t_{1/2} = \frac{0.693}{k}$

Thus `a' does not appear in this equation so that $t_{1/2}$ is independent of a. Similarly, it can be seen that $t_{1/2}$, $t_{2/3}$ etc. will also be independent of the initial concentration.

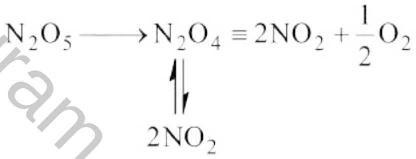
The time taken for half of the reaction to be completed i.e., the time in which the concentration of a reactant is reduced to half of its original value is called Half-life period of the reaction.

The above result can also be used to test a reaction of the first order. The method is called fractional life method.

iii) The units of k are independent of the units in which the concentrations are expressed. This is obvious from equation (5) because in this equation k depends upon the ratio of two concentrations viz. $\frac{a}{a-x}$ and the time t. Thus so long as both a and (a – x) are expressed in the same concentration units, the value of k is not affected. The units of k, therefore, depend only upon the units of time `t'. Depending upon whether t is expressed in second, minutes or hours, k would be in sec^{-1}, min^{-1} or hr^{-1} respectively.

Examples of the Reactions of First Order

1. ***Decomposition of Nitrogen Pentoxide:*** The compound, nitrogen pentoxide, is a volatile solid which decomposes in the gaseous state as well as in the form of its solution in an inert solvent like carbon tetrachloride, chloroform etc. according to the equation.



$$N_2O_5 \longrightarrow \underset{\substack{\upharpoonleft\downharpoonright \\ 2NO_2}}{N_2O_4} \equiv 2NO_2 + \frac{1}{2}O_2$$

When the reaction is carried out in the solution, N_2O_4 and NO_2 remain in the solution and the volume of oxygen gas collected at different intervals of time. It is obvious that

Volume of oxygen gas collected at any time (V_t) left
$\propto$ Amount of N_2O_5 decomposed (x)
i.e.,

$$\left.\begin{array}{l}\text{Volume of oxygen gas collected at} \\ \text{infinite time } (V_\infty) \text{ (which is done by} \\ \text{heating the reaction vessel}\end{array}\right\} \propto \text{Amount of } N_2O_5 \text{ initially}$$

$x \propto V_t$

$a \propto V_\infty$

i.e., Substituting these values in the first order equation viz.

$$k = \frac{2.303}{t}\log\frac{a}{a-x}$$

We get $k = \frac{2.303}{t}\log\frac{V_\infty}{V_\infty - V_t}$

The constancy in the value of k proves the reaction to be of the first order.

Illustration 7: ***For decomposition of N_2O_5 in CCl_4 solution at 320 K***

$2N_2O_5 \longrightarrow 4NO_2 + O_2$

show that the reaction is of first order and also calculate the rate constant:

Time in minutes	***10***	***15***	***20***	***25***	***∞***
Volume of O_2 evolved (in ml)	***6.30***	***8.95***	***11.40***	***13.50***	***34.75***

Solution: If the reaction is of first order, it must obey the equation

$$k = \frac{2.303}{t}\log\frac{a}{(a-x)}$$

In the above reaction, NO_2 remains in solution and oxygen is liberated and collected at different intervals of time.

Therefore, $V_t \propto x$

$V_\infty \propto a$

Substituting these values in the first order equation

$$k = \frac{2.303}{t}\log\frac{a}{a-x} = \frac{2.303}{t}\log\frac{V_\infty}{V_\infty - V_t}$$

Time	V_t	$V_\infty - V_t$	$k = \frac{2.303}{t}\log\frac{V_\infty}{V_\infty - V_t}$
10	6.30	34.75 – 6.30 = 28.45	$k = \frac{2.303}{10}\log\frac{34.75}{28.45} = 0.0198$
15	8.95	34.75 – 8.95 = 25.80	$k = \frac{2.303}{15}\log\frac{34.75}{25.80} = 0.0198$
20	11.40	34.75 – 11.40 = 23.35	$k = \frac{2.303}{200}\log\frac{34.75}{23.35} = 0.0198$
25	13.50	34.75 – 13.50 = 21.25	$k = \frac{2.303}{25}\log\frac{34.75}{21.25} = 0.0198$

Since the value of k comes out to be constant the reaction, therefore, is of first order. The average value of rate constant is 0.0198 min^{-1}.

Decomposition of Hydrogen Peroxide: The decomposition of hydrogen peroxide in aqueous solution (catalysed by the presence of finely divided platinum) takes place according to the equation

$$H_2O_2 \rightarrow H_2O + \frac{1}{2}O_2$$

The kinetics of this reaction may be studied either by the same method as done earlier (i.e. collecting the oxygen gas produced and noting its volume at different intervals of time) or by making use of the fact that H_2O_2 solution can be titrated against $KMnO_4$ solution. Thus by withdrawing equal amounts of the solution (usually 5 cc) at regular intervals of time and titrating against the same $KMnO_4$ solution, the amount of H_2O_2 present can be found every time. It is obvious that for the same volume of the reaction solution withdrawn,

$$\left.\begin{array}{l}\text{Volume of KMnO}_4\text{ solution used}\\ \text{before the commencement of the}\\ \text{reaction i.e. at zero time }(V_0)\end{array}\right\} \propto \left\{\begin{array}{l}\text{Initial concentartion}\\ \text{of H}_2\text{O}_2\text{ (a)}\end{array}\right.$$

i.e., $a \propto V_0$

$$\left.\begin{array}{l}\text{Volume of KMnO}_4\text{ solution used}\\ \text{at any instant of time t }(V_t)\end{array}\right\} \propto \left\{\begin{array}{l}\text{Amount of H}_2\text{O}_2\\ \text{present at that}\\ \text{instant i.e. (a – x)}\end{array}\right.$$

$$(a-x) \propto V_t$$

Substituting these values in the first order equation, we get

$$k = \frac{2.303}{t}\log\frac{a}{a-x}$$

or $$k = \frac{2.303}{t}\log\frac{V_0}{V_t}$$

The decomposition of hydrogen peroxide, as tested by this equation, is found to be of the first order.

Illustration 8: ***From the following data show that the decomposition of an aqueous solution of hydrogen peroxide is of first order:***

Time (minutes)	***0***	***10***	***20***	***30***
V (ml)	***46.1***	***29.8***	***19.6***	***12.3***

where V is the volume of potassium permanganate solution in ml required to decompose a definite volume of the peroxide solution.

Solution: It is evident from the given data that the zero – time titre – value is proportional to the original concentration of hydrogen peroxide, i.e., a. The titre value at any time t corresponds to undecomposed hydrogen peroxide, i.e., (a – x).

Substituting the value in the equation

$$k_1 = \frac{2.303}{t}\log\frac{a}{a-x}, \text{ we get}$$

i) $k_1 = \frac{2.303}{10}\log\frac{46.1}{29.8} = 4.364\times10^{-2}$

ii) $k_1 = \frac{2.303}{20}\log\frac{46.1}{19.6} = 4.276\times10^{-2}$

iii) $k_1 = \frac{2.303}{30}\log\frac{46.1}{12.3} = 4.404\times10^{-2}$

Since k_1 comes out to be constant in the two cases, the reaction is a first order one with the average value of three.

Pseudo Unimolecular Reactions

Consider the following acid-catalysed reactions:

i) Hydrolysis of ethyl acetate

$$\underset{\text{Ethyl acetate}}{CH_3COOC_2H_5} + H_2O \xrightarrow{H^+} \underset{\text{Acetic acid}}{CH_3COOH} + \underset{\text{Ethyl alcohol}}{C_2H_5OH}$$

ii) Inversion of cane-sugar

$$\underset{\text{Sucrose}}{C_{12}H_{22}O_{11}} + H_2O \xrightarrow{H^+} \underset{\text{Glucose}}{C_6H_{12}O_6} + \underset{\text{Fructose}}{C_6H_{12}O_6}$$

Both the above reactions are bimolecular but are found to be of the first order, as experimentally it is observed that

For the first reaction, rate of reaction $\propto$ [$CH_3COOC_2H_5$] only

and for the second reaction Rate of reaction $\propto$ [$C_{12}H_{22}O_{11}$] only.

The reason for such a behaviour is obvious from the fact that water is present in such a large excess that is concentration remains almost constant during the reaction.

Such reactions which are not truly of the first order but under certain conditions become reactions of the first order are called pseudo-unimolecular reactions.

The kinetics of the above reactions have been studied as follows:

1. **Hydrolysis of Ethyl acetate**

$CH_3COOC_2H_5 + H_2O \xrightarrow{H^+} CH_3COOH + C_2H_5OH$

In this reaction acetic acid is one of the products, the amount of which can be found by titration against standard NaOH solution. But being an acid-catalysed reaction, the acid present originally as catalyst, also reacts with NaOH solution. Hence a little careful though reveals that for the same volume of reaction mixture withdrawn at different times.

$$\left.\begin{array}{l}\text{Volume of NaOH solution used in}\\ \text{the beginning i.e. at zero time } (V_0)\end{array}\right\} \propto \left\{\begin{array}{l}\text{Amount of acid present only as catalyst}\\ (\text{as no } CH_3COOH \text{ is produced at } t = 0)\end{array}\right.$$

… (i)

$$\left.\begin{array}{l}\text{Volume of NaOH solution used}\\ \text{at any instant of time t } (V_t)\end{array}\right\} \propto \left\{\begin{array}{l}\text{Amount of acid present as catalyst}\\ + \text{ amount of } CH_3COOH \text{ produced}\end{array}\right.$$

… (ii)

Combining results (i) and (ii), we find that

$$\left.\begin{array}{l}\text{Amount of } CH_3COOH \text{ produced}\\ \text{at any instant of time}\end{array}\right\} \propto (V_t - V_0)$$

… (iii)

$$\left.\begin{array}{l}\text{But amount of } CH_3COOH \text{ produced}\\ \text{at any instant of time}\end{array}\right\} \propto \left\{\begin{array}{l}\text{Amount of } CH_3COOC_2H_5\\ \text{that has reacted (x)}\end{array}\right.$$

Hence $x \propto (V_t - V_0)$ … (iv)

Further

$$\left.\begin{array}{l}\text{Volume of NaOH solution used after the reaction}\\ \text{has taken place for a long time, say 24 hours or so,}\\ \text{called infinite time } (V_\infty)\end{array}\right\} \propto \left\{\begin{array}{l}\text{Amount of acid present as}\\ \text{catalyst + Max. amount}\\ \text{of } CH_3COOH \text{produced}\end{array}\right. \quad \ldots(v)$$

Combining results (i) and (v), we find that

Max. amount of CH_3COOH produced $\propto (V_\infty - V_0)$

But Max. amount of CH_3COOH produced $\propto$

Initial concentration of $CH_3COOC_2H_5$ … (vi)

Hence, a $\propto (V_\infty - V_0)$

From equations (iv) and vi), we have

$$(a - x) \propto (V_\infty - V_0) - (V_t - V_0)$$

or $$(a - x) \propto (V_\infty - V_t) \qquad \ldots \text{(vii)}$$

Substituting the values of a and (a – x) from equations (vi) and (vii) in the first order equation, we get

$$k = \frac{2.303}{t} \log \frac{a}{a - x}$$

or $$\boxed{k = \frac{2.303}{t} \log \frac{V_\infty - V_0}{V_\infty - V_t}}$$

Illustration 9: ***In an experiment to study hydrolysis of an ester 0.5 M HCl at 300 K was used. 5 cm^3 of the reaction mixture was withdrawn after definite intervals and titrated against 0.2 M NaOH solution. Calculate the rate constant at 300K from the following data.***

t (sec)	***0***	***600***	***1200***	***1800***	***∞***
v (cm^3 of NaOH used)	***11.5***	***12.0***	***12.5***	***13.0***	***25.5***

Solution: From the given data, $V_0 = 11.5$ cm^3; $V_\infty = 25.5$ cm^3

$\therefore$ a α $V_\infty - V_0 = 25.5 - 11.5 = 14.0$ and (a – x) α $V_\infty - V_t$

Putting the values of $V_t = 12.0$ at 600 sec.; 12.5 at 1200 sec. and 13.0 at 1800 seconds in the equation

$$k_1 = \frac{2.303}{t} \log \frac{V_\infty - V_0}{V_\infty - V_t}, \text{ we get}$$

i) $$k_1 = \frac{2.303}{600} \log \frac{14.0}{(25.5 - 12.0)} = \frac{2.303}{600} \log \frac{14.0}{13.5} = 6.061 \times 10^{-5}\, s^{-1}$$

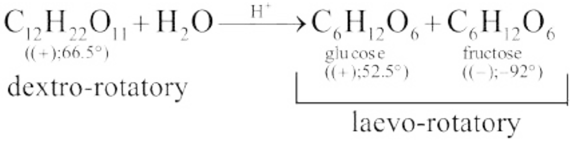
ii) $$k_1 = \frac{2.303}{1200} \log \frac{14.0}{(25.5 - 12.0)} = \frac{2.303}{1200} \log \frac{14.0}{13.0} = 6.176 \times 10^{-5}\, s^{-1}$$

iii) $$k_1 = \frac{2.303}{1800} \log \frac{14.0}{(25.5 - 12.0)} = \frac{2.303}{1800} \log \frac{14.0}{12.5} = 6.296 \times 10^{-5}\, s^{-1}$$

The average value of rate constant $k_1 = 6.177 \times 10^{-5}\, s^{-1}$

Optical Rotation Method

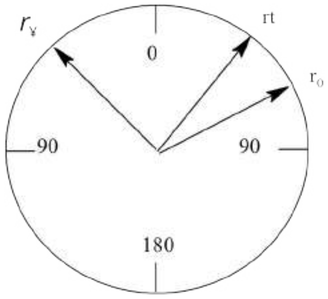
Inversion of Cane Sugar (Sucrose)



$$\underset{\substack{((+);66.5^\circ) \\ \text{dextro-rotatory}}}{C_{12}H_{22}O_{11}} + H_2O \xrightarrow{H^+} \underbrace{\underset{\substack{\text{glucose} \\ ((+);52.5^\circ)}}{C_6H_{12}O_6} + \underset{\substack{\text{fructose} \\ ((-);-92^\circ)}}{C_6H_{12}O_6}}_{\text{laevo-rotatory}}$$

In this reaction by the hydrolysis of dextro-rotatory sucrose produces a mixture of glucose (dextro-rotatory) and fructose (laevo rotatory). As laevo rotation of fructose is more therefore the resulting mixture is laevo rotatory.

The kinetics of above reaction is studied by noting the angle of rotation at different intervals of time using polarimeter.



Say angle of rotation at the start of experiment = r_0
Angle of rotation at any time t = r_t
Angle of rotation at ∞ time = r_∞
Now,
Angle of rotation at any instant of time
= $(r_0 - r_t) \propto$ amount of sucrose hydrolysed
or $x \propto (r_0 - r_t)$
Similarly, angle of rotation at ∝ time
= $(r_0 - r_\infty) \propto$ initial conc. of sucrose (a) or $a \propto (r_0 - r_t)$
Thus, $(a - x) \propto (r_0 - r_\infty) - (r_0 - r_t)$
$\propto (r_t - r_\infty)$
Hence, $k = 2.303 \log \frac{r_0 - r_\infty}{r_t - r_\infty}$

Illustration 10: ***The optical rotation of sucrose in 0.5 N-hydrochloric acid at 308 K and at various time intervals are given below. Find out the rate constant for the first order hydrolysis of sucrose.***

Time (minutes)	***0***	***10***	***20***	***30***	***60***	***∞***
Rotation (degrees)	***+32***	***25.5***	***20.0***	***15.5***	***5.0***	***-10.50***

Solution: Here a, the initial concentration $\propto (r_0 - r_\infty)$
x, the change in time t α $(r_0 - r_t)$
$\therefore (a - x) \propto (r_t - r_\infty)$
Substituting these values for different (a – x) values corresponding to time t from the data in the equation for first order reaction

$$k = \frac{2.303}{t} \log \frac{a}{a-x} = \frac{2.303}{t} \log \frac{r_0 - r_\infty}{r_t - r_\infty}, \text{ we get}$$

i) $k_1 = \frac{2.303}{10} \log \frac{32-(-10.5)}{25.5-(-10.5)} = \frac{2.303}{10} \log \frac{42.5}{36.0} = 0.0166 \text{ min}^{-1}$

ii) $k_1 = \frac{2.303}{20} \log \frac{32-(-10.5)}{20.0-(-10.5)} = \frac{2.303}{20} \log \frac{42.5}{30.0} = 0.0166 \text{ min}^{-1}$

iii) $k_1 = \frac{2.303}{30} \log \frac{32-(-10.5)}{15.5-(-10.5)} = \frac{2.303}{30} \log \frac{42.5}{26.0} = 0.0164 \text{ min}^{-1}$

iv) $k_1 = \frac{2.303}{60} \log \frac{32-(-10.5)}{5.0-(-10.5)} = \frac{2.303}{60} \log \frac{42.5}{15.5} = 0.0168 \text{ min}^{-1}$

Average value of $k_1 = 0.0166 \text{ min}^{-1}$

Half life of nth Order Reaction

$$\begin{array}{lcc} & A \rightarrow & \text{Product} \\ t = 0 & a & 0 \\ t = t & a - x & x \end{array}$$

$$\frac{dx}{dt} \propto (a-x)^n$$

$$\frac{dx}{dt} = K(a-x)^n$$

$$\int_0^{a/2} \frac{dx}{(a-x)^n} = \int_0^{t_{1/2}} K dt$$

Let a – x = z

– dx = dz, when x = 0, z = a

When x = a/2, z = a/2

$$\int_a^{a/2} \frac{-dz}{z^n} = \int_0^{t_{1/2}} K dt \quad \left[\frac{z^{-n+1}}{-n+1}\right]_a^{a/2} = kt_{1/2}$$

$$\frac{a^{1-n}}{n-1}\left[\left(\frac{a}{2}\right)^{1-n} - a^{1-n}\right] = kt_{1/2}$$

$$\frac{1}{a^{n-1}(n-1)}[2^{n-1} - 1] = kt_{1/2}, \; (a^{n-1}).t_{1/2} = \left(\frac{1}{K(n-1)}(2^{n-1} - 1)\right) = k$$

Therefore for a nth order reaction, half life period in inversely related to initial amount

$$\boxed{t_{1/2}a^{n-1} = \text{constant}}$$

Catalyst

Berzelius used the term catalyst for the first time for the substances which accelerate the rate of chemical reaction. Now the term catalyst has been used for the foreign substances which influence the rate of a reaction and the phenomenon is known as catalysis. Usually two terms are used for catalysis:

Positive Catalysis: The phenomenon in which presence of catalyst accelerates the rate of reaction.

Negative catalysis: The phenomenon in which presence of catalyst retards the rate of reaction. Such substances are also known as inhibitors or negative catalyst.

Characteristics of Catalyst

i) A catalyst remains unchanged chemically at the end of reaction, however its physical state may change. e.g. MnO_2 used as catalyst in granular form for the decomposition of $KClO_3$, is left in powder form at the end of reaction.

ii) A catalyst never initiate a chemical reaction. It simply influences the rate of reaction. Exception: combination of H_2 and Cl_2 takes place only when moisture (catalyst) is present.

iii) A small quantity of catalyst is sufficient to influence the rate of reaction e.g. 1 g atom of Platinum is sufficient to catalyse 108 litre of H_2O_2 decomposition.

iv) A catalyst does not influence the equilibrium constant of reaction. It simply helps in attaining equilibrium earlier. It alters the rate of forward & backward reactions equally.

v) A catalyst normally does not alter the nature of products in a reaction. However some exceptions are found to this characteristic.

a) $HCOOH \xrightarrow{AlCl_3} H_2O + CO$, $HCOOH \xrightarrow{Cu} H_2 + CO_2$

b) $CO + 3H_2 \xrightarrow{Ni} CH_4 + H_2O$, $CO + 2H_2 \xrightarrow[Cr_2O_3]{ZnO} CH_3OH$

$CO + H_2 \xrightarrow{Cu} HCHO$

It may therefore be concluded that in some cases nature of products formed depends upon the presence and nature of catalyst used.

vi) A catalyst does not make reaction more exothermic

vii) Catalyst's activity is more or less specific : A catalyst for one reaction is not necessary to catalyse the another reaction.

Types of Catalysis

1. **Homogeneous catalysis:** The reaction in which catalyst and the reactants have same phase. It includes two types.

a) ***Gaseous phase catalysis:*** When reactants and catalyst are in gaseous phase e.g. chamber process for H_2SO_4.

$$2SO_2(g) + O_2(g) \xrightarrow[\text{catalyst}]{NO} 2SO_3(g)$$

b) ***Solution phase catalysis:*** The reactions in which catalyst and reactants are in solution phase or liquid phase of miscible nature.

$$\underset{\text{ester}}{RCOOR'_{(l)}} + H_2O_{(l)} \xrightarrow{H^+} RCOOH + R'OH$$

2. **Heterogeneous catalysis:** The reactions in which catalyst and reactants form phase ≥ 2.

a) ***Solid-liquid catalysis:*** $\left.\begin{array}{l}\text{Reactant : Liquid}\\ \text{Catalyst : Solid}\end{array}\right\}\text{Immiscible}$

$$2H_2O_{2(l)} \xrightarrow[\text{Catalyst}]{MnO_{2(s)}} 2H_2O + O_2$$

b) ***Liquid-Liquid catalysis***: $\left.\begin{array}{l}\text{Reactant : Liquid}\\ \text{Catalyst : Solid}\end{array}\right\}\text{Immiscible}$

$$2H_2O_{2(l)} \xrightarrow[\text{catalyst}]{Hg(l)} 2H_2O + O_2$$

c) ***Solid-gas catalysis:*** $\left.\begin{array}{l}\text{Reactant : gases}\\ \text{Catalyst : solid}\end{array}\right\}\text{Immiscible}$

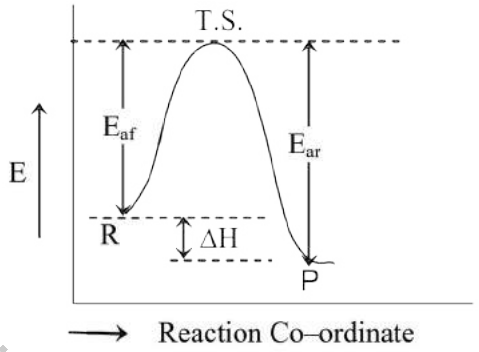
Two aspects of solid catalyst are more significant, one is activity and the other is selectivity. Activity is the ability of catalyst to accelerate chemical reactions; the degree of acceleration can be as high as 10^{10} times in certain reactions. Selectivity is the ability of catalyst to direct reaction to yield particular reaction (excluding others). For example,, n-heptane selectivity gives toluene in presence of Pt catalyst. Similarly $CH_3—CH = CH_2 + O_2$ give $CH_2 = CHCHO$ selectivity over Bismuth molybdate catalyst.

Arrhenius Theory

In 1889 Arrhenius recognised the temperature dependence of rates or rate constant. He has given an emperical relation which can be written as

$$k = Ae^{-E_a/RT} \qquad \dots (1)$$

k is the rate constant (of any order other than zero order), A is the pre-exponential factor, E_a is the activation energy, R is the universal gas constant and T is the absolute temperature. Activation energy (E_a) is the minimum energy required by a reactant at a certain temperature to undergo transformation into product. Arrhenius clearly assumed that reactions occur because of collisions between atoms and molecules of the reactant. He assumed the activation energy to be the least value of energy which the colliding molecules must possess for the collision to yield a product. If we plot graph between activation energy and progress of a reaction (expressed as reaction co-ordinate),we get a graph as shown in figure.



The difference between the energies of the reactant and the transition state (TS) is called E_{a_f}.

$$\Delta H = E_{a_f} - E_{a_r}$$

A, the pre-exponential factor or the frequency factor or the Arrhenius constant is the number of effective collisions occurring per unit time. Effective collision is the number of collisions occurring per unit time in which orientation of the colliding molecules is proper. $e^{-E_a/RT}$ gives the fraction of the effective collision that have the sufficient activation energy. Therefore the product of A and $e^{-E_a/RT}$ gives the number of collisions per unit time that forms the product and is called its number of productive collisions which is the rate constant, k.

For all practical calculations, we shall assume that E_a and A are temperature independent. Both A and E_a are characteristics of the reaction.

Determination of A and E_a

First Method: Taking log of both sides of equation (1)

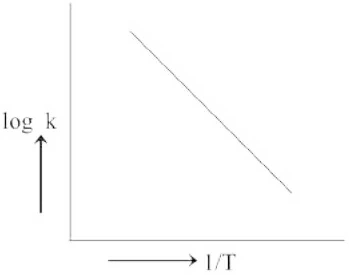
$$\ln k = \ln A - \frac{E_a}{RT}$$

Converting natural log to common log, $\log k = \log A - \frac{E_a}{2.303\ RT}$

If log k is plotted against 1/T, a straight line is obtained which is shown as:

The slope of this line is given by slope $= \frac{-E_a}{2.303\ R}$

Thus, knowing the slope, the E_a can be easily calculated. The intercept of the line will give the value of log A.



Second Method: The logarithmic form of Arrhenius equation is rearranged as

$$\ln k = -\frac{E_a}{RT} + \ln A$$

Differentiating with respect to temperature, we get

$$\frac{d \ln k}{dT} = \frac{E_a}{RT^2}$$

Integrating with in the limits of temperature T_1 and T_2, we get

$$\int_{k_1}^{k_2} d \ln k = \int_{T_1}^{T_2} \frac{E_a}{RT^2} dT$$

$$\ln \frac{k_2}{k_1} = \frac{E_a}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

$$\text{or } \log \frac{k_2}{k_1} = \frac{E_a}{2.303\,R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right) \qquad \ldots (2)$$

Where k_1 and k_2 are rate constants at temperatures T_1 & T_2 respectively. Thus, knowing these values E_a can be calculated. When the value of E_a is known, the value of A can be calculated by substituting its value in equation $k = Ae^{-E_a/RT}$. In equation (2), the value of R has to be inserted in the same unit in which E_a is desired.

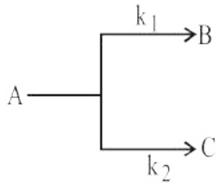
Temperature Coefficient: "Temperature coefficient of a chemical reaction is defined as the ratio of rate constants of a reaction at two temperatures differing by 10°C".

$$\therefore \text{ Temperature coefficient} = \frac{k_{T+10}}{k_T} \text{ » } 2 \text{ to } 3$$

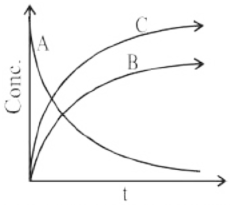
where k_T is the rate constant at temperature T K and k_{T+10} is the rate constant at temperature (T+10) K. This ratio generally falls between 2 and 3 which means for most of the chemical reactions, the rate becomes two or three folds for every 10°C rise in temperature.

Reactions Involving Two First Order Parallel Reactions or Concurrent Reactions

These are reactions in which a reacting substance do not follow a particular path to give a particular set of products. It follows one or more paths to give different products. For example,



The reactant A follows two different paths to form B and C. (The change in concentration of a, B and C is given in figure below)



Change in conc. of A, B and C

Let initial conc. of A = a mol L^{-1} and say the amount transformed in time t = x mol L^{-1}.

If y and z be amounts of B and C formed at time t, then

$$\frac{dx_A}{dt} = \frac{dy_B}{dt} + \frac{dz_C}{dt}$$

Now if the reaction is unimolecular and k_1 and k_2 are rate constants for formation of B and C from A then

rate of formation of y, $\frac{dy_B}{dt} = k_1(a - x);$

and rate of formation of z, $\frac{dz_C}{dt} = k_2(a - x)$

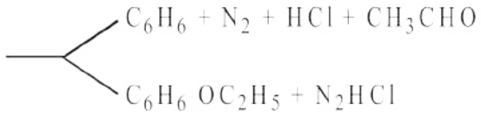
Thus, $\frac{dx_A}{dt} = k_1(a - x) + k_2(a - x) = (k_1 + k_2)(a - x)$

If $k_1 + k_2 = k$, Then $\frac{dx_A}{dt} = k(a - x)$ (Here $r_f B \neq r_f C$)

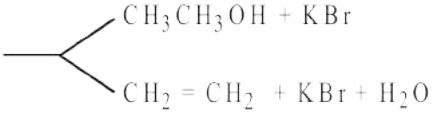
or the rate of reaction will be Rate = k(a – x)

Some examples of side reactions

i) $C_6H_5N = NCl + CH_3CH_2OH$



ii) $CH_3CH_2Br + KOH$



Reactions involving opposing or reversible reactions: Such reactions results in equilibrium. In other words the reactant changes to product and vice versa.

Say we have an opposing reaction in which both forward and backward reactions are first order, viz.,

(k_1 and k_2 are rate constant of forward and backward reaction)
Say initial conc. of A and B are a and b mol L^{-1} respectively.

If after time t, x moles/L of A change into B, then conc. of A and B will be (a – x) and (b + x) respectively.

The net rate of the reaction would be given as :

Rate = $k_1 (a - x) - k_2 (b + x)$ … (i) [∵ both processes occur simultaneously]

When equilibrium is reached, the net rate is zero
Thus, $k_1 (a - x_e) = k_2 (b + x_e)$ (e = equilibrium)

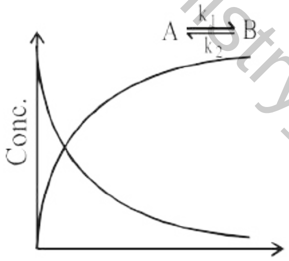
Hence, $(b + x_e) = \frac{k_1}{k_2}(a - x_e)$ or $b = \frac{k_1}{k_2}(a - x_e) - x_e$

Substituting value of b in eqn. (i)

Rate of reaction, $\frac{dx}{dt} = k_1(a - x) - k_2\left[\frac{k_1}{k_2}(a - x_e) - x_e + x\right]$

on solving, we get
Rate = $(k_1 + k_2)(x_e - x)$

After rearranging and integrating the equation, we get an equation similar to first order reaction as shown below.



or $\frac{dx}{x_e - x} = (k_1 + k_2)dt$

$$\int_{x_0}^{x} \frac{dx}{x_e - x} = \int_0^t (k_1 + k_2)dt \text{ or } \log\frac{x_e - x_0}{x_e - x} = (k_1 + k_2)t$$

or $(k_1 + k_2) = \frac{1}{t}\log\frac{x_e - x_0}{x_e - x}$

The equation is similar to first order reaction except that the measured rate constant is now the sum of the forward and the reverse rate constants.

Consecutive or Sequential Reactions

A Typical Example: In many cases, the product formed in one of the elementary reactions acts as the reactant for some other elementary reaction. One of the examples of consecutive reactions involves the following steps.

$$A \xrightarrow{k_1} B \xrightarrow{k_1'} C$$

Let the initial concentration of A be $[A]_0$ and let after time t, the concentrations of A, B and C be [A], [B] and [C], respectively. It is obvious that

$$[A]_0 = [A] + [B] + [C] \qquad \ldots(1)$$

Differential Rate Law: The differential rate expressions are

$$-\frac{d[A]}{dt} = k_1[A] \qquad \ldots(2)$$

$$\frac{d[B]}{dt} = k_1[A] - k_1'[B] \qquad \ldots(3)$$

$$\frac{d[C]}{dt} = k_1'[B] \qquad \ldots(4)$$

On integrating equation (2), we get

$$[A] = [A]_0 e^{-k_1 t} \qquad \ldots(5)$$

Substituting [A] from equation (5) into equation (3), we get

$$\frac{d[B]}{dt} = k_1[A]_0 e^{-k_1 t} - k_1'[B]$$

$$\frac{d[B]}{dt} + k_1'[B] = k_1[A]_0 e^{-k_1 t}$$

Integrated Rate Law: Multiplying the above expression throughout by exp (k'_1t), we get

$$\frac{d[B]}{dt} + k_1'[B]e^{k_1't} = k_1[A]_0 e^{-(k_1-k_1')t}$$

The left side of the above expression is equal to $d([B]e^{k_1't})/dt.$ Hence, the above expression can written as

$$d\{[B]e^{k_1't}\} = k_1[A]_0 e^{-(k_1-k_1')t}dt$$

Integrating the above expression with [B] = 0 at t = 0, we get

$$[B]e^{k't} = k_1[A]_0\left[\frac{e^{-(k_1-k_1')t}}{-(k_1-k_1')} + \frac{1}{k_1-k_1'}\right]$$

$$[B] = k_1[A]_0\left[\frac{e^{-k_1 t}}{-(k_1'-k_1)} + \frac{e^{-k_1't}}{k_1-k_1'}\right]$$

$$[B] = k_1[A]_0\left(\frac{k_1}{k_1'-k_1}\right)\{e^{-k_1 t} - e^{-k_1't}\} \qquad \ldots(6)$$

Substituting equations (5) and (6) in equation (1), we get

$$[A]_0 = [A]_0 e^{-k_1 t} + [A]_0 \left(\frac{k_1}{k_1' - k_1}\right)(e^{-k_1 t} - e^{-k_1' t}) + [C]$$

$$\text{or } [C] = [A]_0 \left[1 - \frac{1}{k_1' - k_1}(k_1' e^{-k_1 t} - k_1 e^{-k_1' t}\right] \qquad \ldots(7)$$

Figure (1) Illustrates the general appearance of the variations of concentrations of A, B and C during the progress of the reaction.

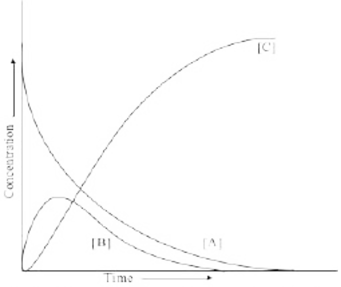


Fig. 1: Typical variations of concentration of A, B and C during the progress of the reaction AB. The actual variations on the values of k_1 and k'.

In general concentration of A decreases exponentially, the concentration of B initially increases upto a maximum and then decreases thereafter, and the concentration of C increases steadily until it reaches its final value $[A]_0$, when all A has changed into C.

Maximum Concentration of B: Equation (6) is

$$[B] = [A]_0 \left(\frac{k_1}{k_1' - k_1}\right)\{e^{-k_1 t} - e^{-k_1' t}\} \qquad \ldots(6)$$

At the maximum concentration of B, we have

$$\frac{d[B]}{dt} = 0$$

Hence, differentiating equation (6) with respect to t, we get

$$\frac{d[B]}{dt} = [A]_0 \left(\frac{k_1}{k_1' - k_1}\right)\{-k_1 e^{-k_1 t} + k_1' e^{-k_1' t}\} \qquad \ldots(8)$$

Equating equation (8) to zero, we get

$$-k_1 e^{-k_1 t_{max}} + k_1' e^{-k_1' t_{max}} = 0$$

$$\text{or} \qquad \frac{k_1}{k_1'} = e^{(k_1 - k_1')t_{max}}$$

$$\text{or} \qquad \ln\left(\frac{k_1}{k_1'}\right) = (k_1 - k_1')t_{max}$$

$$\text{or} \qquad t_{max} = \frac{1}{k_1 - k_1'} \ln\left(\frac{k_1}{k_1'}\right) \qquad \ldots(9)$$

substituting equation (9) in equation (6), we get

$$[B]_{max} = [A]_0 \left(\frac{k_1'}{k_1}\right)^{k_1'/(k_1 - k_1')} \qquad \ldots(10)$$

Pressure Change Method

This method is used for gaseous reactions.
As reaction proceeds there is change in pressure.

For a reaction,	$A_{(g)} \longrightarrow$	$B_{(g)}$ +	$C_{(g)}$
Initial pressure at t = 0	P_0	0	0
Pressure at time (t)	$(P_0 - x)$	x	x

(Here x is no. of moles of A which change to produce)

Thus, total pressure (P_t) at time (t) = $P_0 - x + x + x$

or $\quad P_t = P_0 + x, \qquad x = P_t - P_0$

$\quad a - x = P_0 - (P_t - P_0) = 2P_0 - P_t$

Thus, $k = \frac{2.303}{t} \log \frac{P_0}{(2P_0 - P_t)}$

Illustration 11: ***The following rate data was obtained for the first order thermal decomposition of $SO_2Cl_{2(g)}$ at a constant volume.***

$SO_2Cl_{2(g)} \longrightarrow SO_{2(g)} + Cl_{2(g)}$

Exp.	*Time (sec^{-1})*	*Total pressure (atm)*
1.	*0*	*0.5*
2	*100*	*0.6*

Calculate the reaction rate when total pressure is 0.65 atmosphere.

Solution: Let us say that the pressure of SO_2Cl_2 decreases by x atm, then the increase of pressure of SO_2 and Cl_2 = x atm each. [∵ 1 mole of SO_2Cl_2 decomposes to give 1 mole of SO_2 and 1 mole of Cl_2].

	$SO_2Cl_{2(g)} \longrightarrow$	$SO_{2(g)}$ +	$Cl_{2(g)}$
Pressure at t = 0	0.5 atm	0	0
Pressure at t,	(0.5 – x atm)	x atm	x atm

Since total pressure $(P_T) = P_{SO_2Cl_2} + P_{SO_2} + P_{Cl_2}$

$= (0.5 - x) + x + x$

$P_T = 0.5 + x \;$ or $x = P_T - 0.5$

Hence $\quad P_{SO_2Cl_2} = 0.5 - (P_T - 0.5)$

$= 0.5 - P_T + 0.5 = 1.0 - P_T$

Since, at t = 100 sec, $P_T = 0.6$ atm

∴ $P_{SO_2Cl_2} = 1.0 - 0.6 = 0.4$ atm

a) Evaluation of k

$$k = \frac{2.303t}{t}\log\frac{\text{Initial pressure}}{\text{Pressure at time t}}$$

$$= \frac{2.303}{100}\log\frac{0.5}{0.4} = \frac{2.303}{100}\log 1.25 = \frac{2.303}{100}\times 0.0969 = 2.23 \times 10^{-3}\ \text{sec}^{-1}$$

b) Rate at $P_T = 0.65$ atm

$P_{SO_2Cl_2}$ at total pressure of 0.65 atm = 1.0 – 0.65 = 0.35 atm

Rate = $k[N_2O_5] = 2.23 \times 10^{-3} \times 0.35 = 7.8 \times 10^{-4}$ atm sec^{-1}

Illustration 12: ***The gaseous reaction, $A(g) \longrightarrow 2B(g) + C(g)$ is observed to be the first order. On staring with pure A, it is found that at the end of 10 min, the total pressure of the system is 176 mm of Hg and after a long time, it is 270 mm of Hg. Calculate (a) the initial pressure A (b) the partial pressure of A after 10 min, and (c) the rate constant of the reaction.***

Solution: (a) Let the initial pressure of A be P_0 mm of Hg and the pressure of A decreases in 10 minute be x unit.

	$A(g)$ $\longrightarrow$	$2B(g)$ +	$C(g)$
Initially	P_0	0	0
At time 10 min.	$P_0 - x$	$2x$	x
At ∞ time	0	$2P_0$	P_0

After long time interval, $P_\infty = 2P_0 + P_0 = 3P_0$

$$\therefore \quad P_0 = \frac{P_\infty}{3} = \frac{270}{3} = 90\ mm\ of\ Hg$$

(b) After 10 minutes, $P_t = P_0 + 2x$

$176 = 90 + 2x$

$\therefore$ x = 43 mm of Hg

$\therefore$ Partial pressure of A after 10 min = $P_0 - x = 90 - 43 = 47$ mm of Hg.

(c) For a fist –order reaction, the rate constant expression would be

$$k = \frac{2.303}{t}\log\frac{P_0}{P_0 - x}$$

$$k = \frac{2.303}{10}\log\frac{90}{47} = 0.0649\ \text{min}^{-1}$$

Illustration 13: ***For the reaction, $2NO + H_2 \longrightarrow N_2O + H_2O$ the value of –dp/dt is found to be 1.50 Torr s^{-1} for a pressure of 359 Torr of NO and 0.25 Torr s^{-1} for a pressure of 152 Torr, the pressure of H_2 being constant. On the other hand, when the pressure of NO is kept constant, -dp/dt is 1.60 Torr s^{-1} for a hydrogen pressure of 289 Torr and 0.79 Torr s^{-1} for a pressure of 147 Torr. Determine the order of the reaction***

Solution: Rate law would be represented as

$$\frac{-dp}{dt} = Rate = k[P_{NO}]^a[P_{H_2}]^b$$

Using the date given in the problem, keeping pressure of H_2 constant, we get

$$1.50 = k[359]^a \left[P_{H_2}\right]^b \quad \text{. . . . . (i)}$$

$$0.25 = k[152]^a \left[P_{H_2}\right]^b \quad \text{. . . . (ii)}$$

Dividing (i) by (ii), $\frac{1.50}{0.25} = \left(\frac{359}{152}\right)^a = 6$

Taking log of both sides,

$$\log 6 = a \log\frac{359}{152}$$

$\therefore\ a \approx 2$

Similarly, by keeping the pressure of NO constant, rate law is given by

$$1.60 = k\left[P_{NO}\right]^a\left[289\right]^b \quad \text{. . . . (iii)}$$

$$0.79 = k\left[P_{NO}\right]^a\left[147\right]^b \quad \text{. . . .(iv)}$$

Dividing (iii) by (iv)

$$\frac{1.60}{0.79} = \left(\frac{289}{147}\right)^b$$

Taking log of both sides

$$\log\left(\frac{1.60}{0.79}\right) = b\log\left(\frac{289}{147}\right)$$

$\therefore\ b \approx 1$

$\therefore$ overall order of the reaction = (a + b) = (2 + 1) = 3

Radioactivity

Radioactivity may be defined as a process in which nuclei of certain elements spontaneously disintegrate (transformation into another element by the ejection of α -or β - particle)at a rate characteristic for each particular active isotope (Becquerel, 1896). All the heavy elements from bismuth (atomic number 83) through uranium and also a few of the lighter elements possess radioactive properties. However, the radioactive property of the different radioactive elements differs widely, e.g. radium atoms have about three million times the activity of uranium atoms. Uranium in the form of potassium uranyl sulphate, $KUO_2(SO_4)_2$ was the first compound found to be radioactive. Radioactive changes are spontaneous. These are not controlled by temperature, pressure or nature of chemical combination.

Law of Radioactive Disintegration

i) Atoms of all radioactive elements undergo spontaneous disintegration and form new radioactive elements. The disintegration is accompanied by the emission of α-, β-, or γ-rays.

ii) The disintegration is at random, i.e. every atom has equal chance for disintegration at any time.

iii) The number of atoms that disintegrate per second is directly proportional to the number of remaining unchanged radioactive atoms present at any time. The disintegration is independent of all physical and chemical conditions like temperature, pressure chemical combination etc.

The two laws of radioactive disintegration can be summed up as below:

1. ***Group displacement law:*** The result of α- and β- particle changes can be summed up in the form of group displacement law. *"in an α-particle change the resulting element has an atomic weight less by four units and atomic number less by two units and it falls in a group of the periodic table two columns to the left of the original element, and in a β-particle change the resulting element has same atomic weight but its atomic number is increased by one than its parent and hence it lies one column to right".*

2. ***Law of radioactive decay:*** According to the law of radioactive decay, *the quantity of a radioelement which disappears in unit time (rate of disintegration) is directly proportional to the amount present.*

Determination of the number of α-and β-particles emitted in a nuclear reaction: Consider the following general reaction.

$$ {}^{m}_{n}X \longrightarrow {}^{m'}_{n'}Y + a\,{}^{4}_{2}\alpha + b\,{}^{0}_{-1}\beta $$

Then,

(i) $m = m' + 4a + 0b$ (ii) $n = n' + 2a - b$

Solve for a and b

Where a is the number of ${}^{4}_{2}He$ emitted and b is the number of ${}^{0}_{-1}\beta$ emitted

Points to Remember

1. Rate of decay (activity, A) is the number of atoms undergoing decay to unit time; it is represented by $-\frac{dN_t}{dt}$.

2. Rate of decay of a nuclide is directly proportional to the number of atoms of that nuclide present at that moment, hence.

$$ -\frac{dN_t}{dt} \propto N \text{ or } d\frac{N_t}{dt} = \lambda N_t $$

(the negative sign shows that the number of radioactive atoms, N_t decreases as time t increases)

3. Rate of decay of nuclide is independent of temperature, so its energy of activation is zero.

4. Since the rate of decay is directly proportional to the amount of the radioactive nuclide present and as the number of undecomposed atoms decreases with increase in time, the rate of decay also decreases with the increase in time.

Various forms of equation for radioactive decay are

$$N_t = N_0 e^{-\lambda t}$$

$$\log N_0 - \log N_t = 2.303\lambda t$$

$$\log \frac{N_0}{N_t} = \frac{\lambda t}{2.303}$$

$$\lambda = \frac{2.303}{t} \log \frac{N_0}{N_t} \qquad \text{...(I)}$$

Note that the equation (I) is similar to that of first order reaction, hence we can say that radioactive disintegration are examples of first order reactions.

Where N_0 = Initial number of atoms of the given nuclide, i.e. at time 0
N_t = No. of atoms of that nuclide present after t
λ = Decay constant

However, unlike first order rate constant (K), the decay constant (λ) is independent of temperature.

Decay constant: The ratio between the number of atoms disintegrating in unit time to the total number of atoms present at that time is called the decay constant of that nuclide.

Characteristics of decay constant (λ)

1. It is characteristic of a nuclide (not of an element)
2. Its units are time^{-1}
3. Its value is always less than one

Half-life Period ($T_{1/2}$ or $t_{1/2}$): Rutherford in 1904 introduced a constant known as half-life period of the radio-element for evaluating its radioactivity or for comparing its radioactivity with the activities of other radio-elements. The half-life period of a radio-element is defined as the time required by a given amount of the element of decay to one-half of its initial value.

Mathematically, $T_{1/2} = \frac{0.6932}{\lambda}$

Average Life Period (T): Since total decay period of any element is infinity, it is meaningless to use the term total decay period (total life period) for radio elements. Thus the term average life is used which is determined by the following relation.

$$\text{Average life (T)} = \frac{\text{Sum of lives of the nuclie}}{\text{Total number of nuclei}}$$

Relation between average life and half-life. Average life (T) of an element is the inverse of its decay constant i.e.,

$$T = \frac{1}{\lambda}$$

Substituting the value of λ in the above equation,

$$T = \frac{T_{1/2}}{0.693} = 1.44T_{1/2}$$

Thus, Average life (T) = 1.44 × Half-life ($T_{1/2}$) = $\sqrt{2} \times T_{1/2}$

Thus the average life period of a radioisotope is approximately under-root two times of its half life period.

Specific activity: It is the measure of radioactivity of a radioactive substance. It is defined as 'the number of radioactive nuclei which decay per second per gram of radioactive isotope'. Mathematically, if 'm' is the mass of radioactive isotope, then

$$\text{Specific activity} = \frac{\text{Rate of decay}}{m} = \frac{\lambda N}{m} = \lambda \times \frac{\text{Avogadro number}}{\text{Atomic mass in g}}$$

Where N is the number of radioactive nuclei, which undergoes disintegration.

Solved Problems

Objective

Problem 1: ***What is the activation energy for the decomposition of N_2O_5 as***

$$N_2O_5 \rightleftharpoons 2NO_2 + \frac{1}{2}O_2$$

If the values of the rate constants are 3.45×10^{-5} and 6.9×10^{-3} at 27°C and 67°C respectively.

(a) 102×10^2 kJ ***(b) 488.5 kJ***
(c) 112 kJ ***(d) 112.5 kJ***

Solution:

$$\log\frac{K_2}{K_1} = \frac{Ea}{2.303R}\left[\frac{T_2 - T_1}{T_1T_2}\right]$$

$$\log\frac{6.9\times10^{-3}}{3.45\times10^{-5}} = \frac{Ea}{2.303\times8.31}\left[\frac{40}{300\times400}\right]$$

Ea = 112.5 kJ

∴ **(d)**

Problem 2: ***The kinetic datas for the reaction: $2A + B_2 \longrightarrow 2AB$ are as given below:***

[A]	***[B_2]***	***Rate***
mol L^{-1}	***mol L^{-1}***	***mol L^{-1} min^{-1}***
0.5	***1.0***	***2.5×10^{-3}***
1.0	***1.0***	***5.0×10^{-3}***
0.5	***2.0***	***1×10^{-2}***

Hence the order of reaction w.r.t. A and B_2 are, respectively,

(a) 1 and 2 ***(b) 2 and 1***
(c) 1 and 1 ***(d) 2 and 2***

Solution:

$2.5 \times 10^{-3} = K[0.5]^{\alpha}[1.0]^{\beta}$ …(1)

$5 \times 10^{-3} = K[1.0]^{\alpha}[1.0]^{\beta}$ …(2)

$1 \times 10^{-2} = K[0.5]^{\alpha}[2.0]^{\beta}$ …(3)

Dividing equation (1) and (2)

$$\frac{1}{2} = \left[\frac{1}{2}\right]^{\alpha}$$

hence $\alpha = 1$

Dividing equation (1) and (3)

$$\frac{2.5\times10^{-3}}{1\times10^{-2}} = \left(\frac{1.0}{2.0}\right)^{\beta}$$

$$\frac{1}{4} = \left(\frac{1}{2}\right)^{\beta}$$

$\beta = 2$ ∴ **(a)**

Problem 3: ***For the first order reaction $A_{(g)} \rightarrow 2B_{(g)} + C_{(g)}$, the initial pressure is $P_A = 90$ mm Hg, the pressure after 10 minutes is found to be 180 mm Hg. The rate constant of the reaction is***

(a) 1.15×10^{-3} sec^{-1} ***(b) 2.3×10^{-3} sec^{-1}***

(c) 3.45×10^{-3} sec^{-1} ***(d) 6×10^{-3} sec^{-1}***

Solution: $A \rightarrow 2B + C$
$P \quad 0 \quad 0$
$P - x \quad 2x \quad x$
At equilibrium
$180 = P - x + 2x + x$
$180 = 90 + 2x$
$2x = 90,\ x = 45$

$$K = \frac{2.303}{t}\log\frac{P}{P-x} = \frac{2.303}{10}\log\frac{90}{90-45} = \frac{2.303}{10}\log 2 = \frac{0.6932}{10}$$

$$= 0.6932 = \frac{0.06932}{60} = 1.1555 \times 10^{-3}\ \text{sec}^{-1}$$

$\therefore$ **(a)**

Problem 4: ***In the reaction $2N_2O_5 \longrightarrow 4NO_2 + O_2$, $+\frac{d[NO_2]}{dt}$ at any time t was found to be 2.4×10^{-4} mole L^{-1} min^{-1} with rate constant 4.4×10^{-4} min^{-1}. Hence $-\frac{d[N_2O_5]}{dt}$ at the same time t and the corresponding rate constant of the reactions respectively would be***

(a) 1.2×10^{-4} mole L^{-1} min^{-1} and 2.2×10^{-4} min^{-1}
(b) 1.2×10^{-4} mole L^{-1} min^{-1} and 8.8×10^{-4} min^{-1}
(c) 4.8×10^{-4} mole L^{-1} min^{-1} and 2.2×10^{-4} min^{-1}
(d) 2.4×10^{-4} mole L^{-1} min^{-1} and 4.4×10^{-4} min^{-1}

Solution: For 4 moles of NO_2 formed, 2 moles of N_2O_5 consumed in a given time interval, so the rate consumption of N_2O_5 must be half of the rate of formation of NO_2. Rate constants w.r.t. these two rates will also have the same relationship. So, the choice (A) is the correct answer.

Problem 5: ***The reaction : $2NO + 2H_2 \longrightarrow N_2 + 2H_2O$ has been assigned to follow following mechanism.***

I. $NO + NO \rightleftharpoons N_2O_2$ (fast)
II. $N_2O_2 + H_2 \longrightarrow N_2O + H_2O$ (slow)
III. $N_2O + H_2 \longrightarrow N_2 + H_2O$ (fast)

The rate constant of step II is 1.2×10^{-4} mole^{-1} L. min^{-1} while equilibrium constant of step I is 1.4×10^{-2}. What is the rate of reaction when concentration of NO and H_2 each is 0.5 mole L^{-1}

(a) 2.1×10^{-7} mole L^{-1} min^{-1} ***(b) 3.2×10^{-6} mole L^{-1} min^{-1}***

(c) 3.5×10^{-4} mole L^{-1} min^{-1} ***(d) none of these***

Solution: $k_{obs} = k.k_c = 1.2 \times 10^{-1} \times 1.4 \times 10^{-2} = 1.68 \times 10^{-6}$ mole^{-1} L min^{-1}

Rate = k_{obs} $[NO]^2$ $[H_2]$
$= 1.68 \times 10^{-6} \times 0.5^2 \times 0.5$
$= 2.1 \times 10^{-7}$ mole L^{-1} min^{-1}
So, answer must be choice (a)

Problem 6: ***A first order reaction : A $\longrightarrow$ Products and a second order reaction: 2R $\longrightarrow$ Products both have half - time of 20 minutes when they are carried out taking 4 mole L^{-1} of their respective reactants. Number of mole per litre of A and R remaining unreacted after 60 minutes from the start of the reaction, respectively will be.***

(a) 1 and 0.5 ***(b) 0.5 and negligible***
(c) 0.5 and 1 ***(d) 1 and 0.25***

Solution: In the case of first order reaction $t_{1/2}$ will remain constant independent of initial concentration so.

4mole L^{-1} $\xrightarrow{20\,min}$ 2mole L^{-1} $\xrightarrow{20\,min}$ 1mole L^{-1} $\xrightarrow{20\,min}$ 0.5 moile L^{-1}.

That is, after 60 minutes 0.5 mole L^{-1} of A will be left unreacted.

In the case of second order reaction $t_{1/2}$ is inversely proportional to initial concentration of reactant i.e., $t_{1/2}$ will go on doubling as concentration of reactant will go on getting half. That is, $t_{1/2}$ a will be constant, so.

4 mole L^{-1} $\xrightarrow{20\,min}$ 2 mole L^{-1} $\xrightarrow{40\,min}$ 1 mole L^{-1}.

That is, after 60 minutes, the concentration of R remaining unreacted will be 1 mole L^{-1}. Note that $t_{1/2}$ a = $20 \times 4 = 40 \times 2 = 80$ mole L^{-1} min, a constant.

$\therefore$ **(b)**

Problem 7: ***Two substances A and B are present such that $[A_0] = 4[B_0]$ and half–life of A is 5 minute and that of B is 15 minute. If they start decaying at the same time following first order kinetics how much time later will the concentration of both of them would be same.***

(a) 15 minute ***(b) 10 minute***
(c) 5 minute ***(d) 12 minute***

Solution: Amount of A left in n_1 halves = $\left(\frac{1}{2}\right)^{n_1} [A_0]$

Amount of B left in n_2 halves = $\left(\frac{1}{2}\right)^{n_2} [B_0]$

At the end, according to the question

$$\frac{[A^0]}{2^{n_1}} = \frac{[B_0]}{2^{n_2}} \Rightarrow \frac{4}{2^{n_1}} = \frac{1}{2^{n_2}}, \ \left[[A_0] = 4[B_0]\right]$$

$$\therefore \frac{2^{n_1}}{2^{n_2}} = 4 \Rightarrow 2^{n_1 - n_2} = (2)^2 \therefore n_1 - n_2 = 2$$

$$\therefore n_2 = (n_1 - 2) \qquad \ldots(1)$$

Also $t = n_1' \ t_{1/2(A)}$ $\ t = n_2 \times t_{1/2(B)}$

(Let concentration of both become equal after time t)

$\backslash \; \frac{n_1 \text{´} \; t_{1/2(A)}}{n_2 \text{´} \; t_{1/2(B)}} = 1 \;\text{Þ}\; \frac{n_1 \text{´} \; 5}{n_2 \text{´} \; 15} = 1 \;\text{Þ}\; \frac{n_1}{n_2} = 3$ …(2)

For equation (1) and (2)

$n_1 = 3, n_2 = 1$

$t = 3 \times 5 = 15$ minute

$\therefore$ **(a)**

Problem 8: ***Fill in the blank***

$^{235}_{92}U + ^{1}_{0}n \longrightarrow ? + ^{92}_{36}Kr + 3^{1}_{0}n$

(a) $^{141}_{56}Ba$ *(b)* $^{139}_{56}Ba$

(c) $^{139}_{54}Ba$ *(d)* $^{141}_{54}B$

Solution: $92 + 0 = Z + 36 + 0 \Rightarrow Z = 56$

$235 + 1 \longrightarrow A + 92 + 3$

$\therefore\ A = 144$

Missing nuclide is $^{141}_{56}Ba$

$\therefore$ **(a)**

Problem 9: ***The reaction A(g) + 2B(g) → C(g) + D(g) is an elementary process. In an experiment, the initial partial pressure of A and B are $P_A = 0.60$ and $P_B = 0.80$atm. When $P_C = 0.2$atm the rate of reaction relative to the initial rate is***

(a) 1/48 ***(b) 1/24***

(c) 9/16 ***(d)1/6***

Solution: $R_1 = K[A][B] \;\; = K[0.6][0.80]^2$

After reaction

$$\begin{array}{lllllll} A & + & 2B & \rightarrow & C & + & D \\ 0.6-0.2 & & 0.8-0.4 & & 0.2 & & 0.2 \\ 0.4 & & 0.4 & & 0.2 & & 0.2 \end{array}$$

$$\frac{R_2}{R_1} = \frac{K(0.4)(0.4)^2}{(0.6)(0.8)^2} = \frac{1}{6}$$

$\therefore$ **(d)**

Problem 10: ***Thermal decomposition of a compound is of first order. If 50% of a sample of the compound is decomposed in 120 minute show long will it take for 90% of the compound to decompose?***

(a) 399 min ***(b) 410 min***

(c) 250 min ***(d) 120 min***

Solution: $K = \frac{0.6932}{120}$ …(1)

$K = \frac{2.303}{t}\log\frac{a}{0.10a}$

$= \frac{2.303}{t}\log 10$ …(2)

Equating (1) and (2)

$\frac{0.6932}{120} = \frac{2.303}{t}$

t = 399 minutes

$\therefore$ **(a)**

Other Engg. Exams

Problem 11. ***For a given reaction $3A + B \rightarrow C + D$ the rate of reaction can be represented by***

(a) $-\frac{1}{3}\frac{d[A]}{dt} = \frac{-d[B]}{dt} = \frac{+d[C]}{dt} = \frac{+d[D]}{dt}$ ***(b)*** $-\frac{1}{3}\frac{d[A]}{dt} = \frac{d[C]}{dt} = K[A]^m[B]^n$

(c) $+\frac{1}{3}\frac{d[A]}{dt} = \frac{-d[C]}{dt} = K[A]^n[B]^m$ ***v*** ***(d) none of these***

Solution : **(a)** $-\frac{1}{3}\frac{d[A]}{dt} = -\frac{d[B]}{dt} = \frac{+d[C]}{dt} = \frac{+d[D]}{dt}$

Problem 12. ***Which reaction characteristics are changing by the addition of a catalyst to a reaction at constant temperature***

(a) Activation energy ***(b) Equilibrium constant***

(c) Reaction entropy ***(d) Reaction enthalpy***

Solution : **(a)** Catalyst affect only activation energy. It brings down the activation energy of reaction.

Problem 13. ***In the reaction $2N_2O_5 \rightarrow 4NO_2 + O_2$, initial pressure is 500 atm and rate constant K is 3.38×10^{-5} sec^{-1}. After 10 minutes the final pressure of N_2O_5 is***

(a) 490 atm ***(b) 250 atm***

(c) 480 atm ***(d) 420 atm***

Solution: **(a)** $p_0 = 500$ atm

$K = \frac{2.303}{t}\log_{10}\frac{p_0}{p_1}$

$3.38 \times 10^{-5} = \frac{2.303}{10 \times 60}\log\frac{500}{p_t}$

or $0.00880 = \log\frac{500}{p_t} \Rightarrow \frac{500}{1.02} = 490\,atm$

Problem 14. ***In a first order reaction the concentration of reactant decreases from 800mol/dm^3 to 50 mol/dm^3 in 2×10^2 sec. The rate constant of reaction in sec^{-1} is***

(a) 2×10^4 ***(b) 3.45×10^5***

(c) 1.386×10^{-2} ***(d) 2×10^{-4}***

Solution : **(c)** $k = \frac{2.303}{t}\log_{10}\frac{a}{a-x}; t = 2\times10^2, a = 800, a-x = 50$

$$k = \frac{2.303}{2\times10^2}\log_{10}\frac{800}{50} = \frac{2.303}{2\times10^2}\log_{10}16$$

$$= \frac{2.303}{2\times10^2}\log_{10}2^4 = \frac{2.303}{2\times10^2}\times4\times0.301$$

$$= 1.38\times10^{-2}\ s^{-1}$$

Problem 15. ***Rate constant for a reaction H_2 + I_2 □ □□ 2HI is 49, then rate constant for reaction 2HI □ □□ H_2 + I_2 is***

(a) 7 ***(b) 1/49***

(c) 49 ***(d) 21***

Solution : **(b)** For reversible reaction rate constant is also reverse.

Problem 16. ***A reaction that is of the first order with respect to reactant A has a rate constant 6 min^{-1}. If we start with [A] = 0.05 mol l^{-1}, when would [A] reach the value 0.05 mol l^{-1}***

(a) 0.384 min ***(b) 0.15 min***

(c) 3 min ***(d) 3.84 min***

Solution : **(a)** We know that for first order kinetics

$$k = \frac{2.303}{t}\log\frac{a}{a-x}$$

(a – x) = 0.05 mol l^{-1}, $6 = \frac{2.303}{t}\log\frac{0.5}{0.05}$

or $t = \frac{2.303}{6}\log\frac{0.5}{0.05} = \frac{2.303}{6} = 0.384\,\text{min}$

Problem 17. ***A photon of hard gamma radiation knocks a proton out of ${}^{24}_{12}Mg$ nucleus to form***

(a) The isotope of parent nucleus ***(b) The isobar of parent nucleus***

(c) the nuclide ${}^{23}_{11}Na$ ***(d) The isobar of ${}^{23}_{11}Na$***

Solution : **(c)** ${}^{24}_{12}Mg + \gamma \longrightarrow {}^{23}_{11}Na + {}^{1}_{1}\mathrm{H}$

Problem 18. ***A freshly prepared radioactive source of half-life 2 hours emits radiations of intensity which is 64 times the permissible safe level. The minimum time after which it would be possible to work safely with this source is***

(a) 6 hours ***(b) 12 hours***

(c) 24 hours ***(d) 128 hours***

Solution : ***(b)*** $N = \frac{N_0}{64} = \frac{N_0}{2^6} \quad \therefore n = 6$

Thus total time = 2 × 6 = 12 hr.

Problem 19. ***During a negative β-decay***

(a) An atomic electron is ejected

(b) An electron which is already present within the nucleus is ejected

(c) A neutron in the nucleus decays emitting an electron

(d) A part of the binding energy of the nucleus is converted into an electron

Solution : **(c)** β-decay occurs by the nuclear change $n \rightarrow p + {}_{-1}e^0$.

Problem 20. ***The decay constant of a radioactive sample is 'λ'. The half-life and mean life of the sample are respectively***

(a) $\frac{1}{\lambda}, \frac{\ln 2}{\lambda}$ ***(b)*** $\frac{\ln 2}{\lambda}, \frac{1}{\lambda}$

(c) $\lambda \ln 2, \frac{1}{\lambda}$ ***(d)*** $\frac{\lambda}{\ln 2}, \frac{1}{\lambda}$

Solution : **(b)** $t_{1/2} = \frac{\log_e 2}{\lambda}$, Average life = $\frac{1}{\lambda}$

Problem 21. ***Which of the following statements are correct about half-life period.***

(a) it is proportional to initial concentration for zeroth order

(b) Average life = 1.44 half-life for first order reaction

(c) Time of 75% reaction is thrice of half-life period in first order reaction

(d) 99.9% reaction takes place in 100 minutes for the case when rate constant is 0.0693 min^{-1}

Solution : **(a, b, d)**

(a) $t_{1/2} \propto \frac{1}{a^{n-1}}$; (b) $T = \frac{1}{\lambda} = \frac{t_{1/2}}{0.693} = 1.44 t_{1/2}$; (c) $t_{3/4} = 2t_{1/2}$;

(d) $t_{99.9\%} = 10t_{1/2} = 10\left(\frac{0.693}{0.0693}\right) = 100\,\text{min}$

Problem 22. $Zn + 2H^+ \longrightarrow Zn^{2+} + H_2$

Half-life period is independent of concentration of zinc at constant pH. For the constant concentration of Zn, rate becomes 100 times when pH is decreased from 3 to 2. Hence

(a) $\frac{dx}{dt} = k[Zn]^0[H^+]^2$

(b) $\left(\frac{dx}{dt}\right) = k[Zn][H^+]^2$

(c) rate is not affected if concentration of zinc is made four times and that of H^+ ion is halved.

(d) rate becomes four times if concentration of H^+ ion is doubled at constant Zn concentration.

Solution : **(b, c, d)**

for first order reaction, half-life is independent of initial concentration.

$$\frac{dx}{dt} = K\left[H^+\right]^{\alpha}\left[Zn\right] = K'\left[Zn\right]$$

$$\therefore \quad K' = K\left[H^+\right]^{\alpha}$$

$$100 = \frac{10^{-2\alpha}}{10^{-3\alpha}}$$

$\therefore$ $\alpha = 2$

Problem 23. ***The rate law for the reaction : $RCl + NaOH \longrightarrow ROH + NaCl$***

Is given by: rate = k [RCl]. The rate of this reaction

(a) is doubled by doubling the concentration of NaOH

(b) is halved by reducing the concentration of RCl by one half

(c) is increased by increasing the temperature of the reaction

(d) is unaffected by change in temperature

Solution : **(b, c)**

Since order with respect to RCl is one , rate is halved on reducing [RCl] to half . Rage of reaction increases with increase in temperature.

Problem 24. ***For a first order reaction***

(a) The degree of dissociation is equal to $1 - e^{-kt}$

(b) A plot of reciprocal of concentration of reactant vs. time gives a straight line

(c) The time taken for the completion of 75% of reaction is thrice $t_{1/2}$ of the reaction

(d) The pre-exponential factor in the Arrhenius equation has the dimensions of time.

Solution : **(a), (b)**

$$K = \frac{1}{t}\ln\frac{1}{1-\alpha} \Rightarrow -Kt = \ln(1-\alpha)$$

$\therefore$ $\alpha = 1 - e^{-kt}$

Problem 25. ***Taking the reaction, $A + 2B \longrightarrow$ Products, to be of second order, which of the following are the correct rate law expressions?***

(a) $\frac{dx}{dt} = k[A][B]$

(b) $\frac{dx}{dt} = k[A][B]^2$

(c) $\frac{dx}{dt} = k[A]^2$

(d) $\frac{dx}{dt} = k_1[A] + k_2[B]^2$

Solution : **(a), (c)**

The sum of exponents to which the concentration terms are raised should be equal to two.

Problem 26. ***Match column – I with Column - II***

Column – I	***Column - II***
(a) Decomposition of H_2O_2	***$10t_{1/2}$***
(b) $\frac{k_{308}K}{k_{298}K}$	***(q) 1^{st} order***
(c) Arrhenius	***(r) Temperature coefficient***
(d) $t_{99.9\%}$	***(s)*** $\log\frac{k_2}{k_1}=\frac{E_a}{2.303R}\left(\frac{T_2-T_1}{T_1T_2}\right)$
	(t) 2 to 3

Solution : **(a – q) :** Decomposition of H_2O_2 follows 1st order kinetics.

(b – r, t) : Temperature coefficient is ratio of rate constants at 308 K and 298 and it lines between 2 and 3

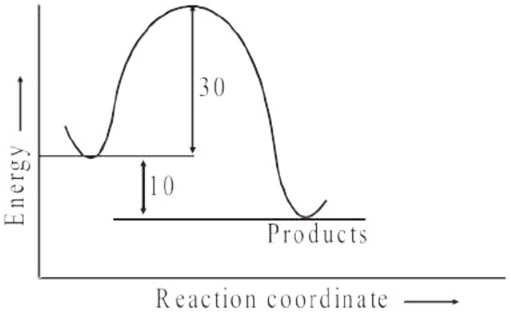
(c – s) : $\log\frac{k_2}{k_1}=\frac{E_a}{2.303R}\left(\frac{T_2-T_1}{T_1T_2}\right)$ is Arrhenius equation

(d - p) : $t_{99.9\%} = 10t_{1/2}$

$$t_{99.9\%} = \frac{2.303}{k}\log\frac{R}{R_0\times\frac{0.1}{100}} = \frac{2.303}{k}\times\log 1000 = \frac{2.303\times 3}{k} = \frac{6.909}{k}$$

$$t_{99.0\%} = 10t_{1/2} = \frac{10\times 0.693}{k} = \frac{6.93}{k}$$

Write-up – I



The above graph represents the energy profile diagram for a 1st order reaction taking place at a constant temperature of 47^0C. The specific rate constant for the forward and backward reaction is 10^{-4} min^{-1} and 10^{-6} min^{-1} respectively.

1. The energy of activation for the backward reaction is :
   (a) 30 kJ mol^{-1} (b) 20 kJ mol^{-1}
   (c) 10 kJ mol^{-1} (d) 40 kJ mol^{-1}

2. In overall reaction heat is
   (a) liberated (b) absorbed
   (c) no change in heat (d) cannot be predicted

3. The maximum rate constant for the forward reaction is
   (a) 5.46 (b) 7.94
   (c) 1.23 (d) 9.83

Solution :

1. **(d)** : $(E_a)_b = 30 + 10 = 40$ KJ/mole

2. **(a)** : $\Delta H = -10$
   exothermic

3. **(b)** : max. rate constant A_f

$$A_f = \frac{K_f}{e^{-(E_a)_f/RT}} = 7.94$$

Write-up – II

Ozone is prepared in laboratory by passing silent electric discharge through pure and dry oxygen in an apparatus known as ozoniser. This conversion from oxygen to ozone is a reversible and endothermic reaction. When oxygen is subjected to an ordinary electric discharge, most of the O_3 produced will get decomposed. When any insulating material such as glass, is inserted in the space between the two electrodes and high current density is applied, silent electric discharge passes on between the two electrodes. By this process no spark is produced and much less heat is generated, and as a result the decomposition of the produced ozone is much retarded.

The decomposition of ozone is believed to occur by the following mechanism:

$O_3 \underset{K_b}{\overset{K_f}{\rightleftharpoons}} O_2 + O$ (fast step)

$O_3 + O \xrightarrow{K_f} 2O_2$ (Slow)

1. Order of the reaction is
(a) 1 (b) 2
(c) 3 (d) 0

2. Molecularity of reaction is defined by
(a) slow step (b) reversible step
(c) from overall reaction (d) fast step

3. When the concentration of O_2 is increased, for the same concentration of ozone, its rate
(a) increases (b) decreases
(c) remains the same (d) cannot be answered

4. When the concentration of O_3 is increased, for the same concentration of oxygen, its rate
(a) increases (b) decreases
(c) remains the same (d) cannot be answered

Solution :

1. **(a)** : Rate = $K_f[O_3]\,[O]$

$$K_e = \frac{[O_2][O]}{[O_3]}$$

$$[O] = \frac{K_e[O_3]}{[O_2]}$$

2. **(a)** : Rate = $K_fK_e[O_3]^2\,[O_2]^{-1}$

3. **(b)** : Rate = $K^1[O_3]^2\,[O_2]^{-1}$
it means as conc. of O_2 increases rate decreases

Subjective

Problem 1: ***At 1100, K, the following data were obtained on the homogeneous reaction:***

$2NO(g) + 2H_2(g) \longrightarrow N_2(g) + 2H_2O\,(g)$

	[NO] (mole dm^{-3})	*[H$_2$] (mole dm^{-3})*	*Rate, r(mole dm^{-3} s^{-1})*
1)	*5×10^{-3}*	*2.5×10^{-3}*	*3×10^{-5}*
2)	*15×10^{-3}*	*2.5×10^{-3}*	*9×10^{-5}*
3)	*15×10^{-3}*	*10×10^{-3}*	*3.6×10^{-5}*

(i) ***Calculate the order of the reaction with respect to NO, with respect to H_2 and the overall reaction order.***

(ii) ***Write the rate law expression for the reaction.***

(iii) ***Calculate the rate constant of the reaction.***

(iv) ***What will be the initial rate of the reaction if [NO] = [H$_2$] =8×10^{3} mole dm^{-3}?***

Solution: i) Let the rate r be equal to $r = k[NO]^a\,[H_2]^b$

where a and b are the order with respect to NO and H_2

Dividing (1) by (2)

$$\frac{3\times10^{-5}}{9\times10^{-5}} = \left(\frac{5\times10^{-3}}{15\times10^{-3}}\right)^a\left(\frac{2.5\times10^{-3}}{2.5\times10^{-3}}\right)^b \Rightarrow \frac{1}{3} = \left(\frac{1}{3}\right)^a \qquad \therefore\ a=1$$

Dividing (2) by (3)

$$\frac{9\times10^{-5}}{3.6\times10^{-5}} = \left(\frac{2.5\times10^{-3}}{10\times10^{-3}}\right)^b \qquad 0.25=(0.25)^b \quad \therefore\ b=1$$

ii) $r = k[NO]\,[H_2]$

iii) $$k = \frac{(3\times10^{-5})}{(5\times10^{-3})(2.5\times10^{-3})}\,dm^3\,mol^{-1}\,s^{-1} = 2.4\,dm^3\,mol^{-1}\,s^{-1}$$

iv) Initial rate = $(2.4)(8\times10^{-3})\,(8 \times 10^{-3})$ mol dm^{-3} s^{-1}

= 1.536×10^{-4} mol dm^{-3} s^{-1}

Problem 2: ***Rate of a reaction A + B → Products; is given below as a function of different initial concentrations of A and B***

[A] mol/litre	*[B] mol litre^{-1}*	*Initial rate mol litre^{-1} time^{-1}*
0.01	*0.01*	*0.005*
0.02	*0.01*	*0.010*
0.01	*0.02*	*0.005*

Determine the order of the reaction with respect to A and with respect to B. What is the half life of A in the reaction?

Solution: Let order with respect to A is m and with respect to B is `n'.

Rate = $K[A]^m\,[B]^n$

$0.005 = K\,[0.01]^m\,[0.01]^n$ … (i)

$0.010 = K\,[0.02]^m\,[0.01]^n$ … (ii)

$0.005 = K[0.01]^m\,[0.02]^n$ … (iii)

Dividing Eq. (i) by (ii), we get

$$\frac{0.005}{0.010} = \left[\frac{0.01}{0.02}\right]^m$$

$$\frac{1}{2} = \left[\frac{1}{2}\right]^m \qquad \therefore\ m = 1$$

Thus, order with respect to A is one.

Dividing Eq. (i) by (ii), we get

$$\frac{0.005}{0.005} = \left[\frac{0.01}{0.02}\right]^n$$

$$1 = \left[\frac{1}{2}\right]^n \qquad \therefore\ n = 0$$

Thus, order with respect to B is zero.

Substituting the values of m and n in Eq. (i), we get

$$0.005 = K\,[0.01]^1\,[0.01]^0 \qquad \therefore\ \frac{0.005}{0.01} = 0.5$$

$$t_{1/2}\,\text{(Half life period)} = \frac{0.693}{K} = \frac{0.693}{0.5} = 1.386 \text{ time}$$

Problem 3: ***The reaction 2A + B + C → D + 2E; is found to be first order in A; second order in B and zero order in C.***

i) Give the rate law for the above reaction in the form of a differential equation.

ii) What is the effect on the rate of increasing the concentration of A, B and C two times?

Solution: i) The rate law according to given information may be given as,

$$\frac{dx}{dt} = K[A]^1[B]^2[C]^0$$

ii) When concentration of A, B and C are doubled then rate will be

$$\frac{dx}{dt} = K[2A][2B]^2[C]^0$$

$$= 8K[A][B]^2[C]^0$$

i.e., rate becomes 8 fold, the original rate.

Problem 4: ***At 27°C it was observed, during a reaction of hydrogenation that the pressure of H_2 gas decreases from 2 atm to 1.1 atm in 75 min. Calculate the rate of reaction (molarity/sec). Given ($R = 0.082$/litre atom K^{-1} mole^{-1})***

Solution: Rate $= \dfrac{\text{Decrease in pressure}}{\text{Time duration}}$

$$= \frac{2-1.1}{75} = 0.012 \text{ atm/min}$$

Rate in atm/sec $= \dfrac{0.012}{60} = 2 \times 10^{-4}$ atm/sec.

Answer is required in molarity per second

$\therefore$ PV = nRT

$$\frac{P}{RT} = \frac{n}{V}$$

$$\frac{P/\sec}{RT} = \left(\frac{n}{V}\right)/\sec$$

$\left(\frac{n}{V}\right)/$ sec = molarity per second

$$\frac{2 \times 10^{-4}}{0.0821 \times 300} = \left(\frac{n}{V}\right)/\sec$$

8.12×10^{-6}. Rate in molarity/sec = (n/V)/sec

Problem 5: ***For the decomposition of dimethyl ether, A in the Arrhenious equation $K = Ae^{-E/RT}$ has a value of 1.26×10^{13} and E_a value of 58.5 kcal. Calculate half life period for first order decomposition at 527°C.***

Solution: Taking logarithm of Arrheniuos equation

$K = Ae^{-E/RT}$ we get

$$\log K = \log A - \frac{E}{2.303RT} \qquad \dots \text{(i)}$$

Given $A = 1.26 \times 10^{13}$

E = 58.5 kcal

T = 527 + 273 = 800 K

Substituting these value in Eq. (i), we get

$$\log K = \log (1.26 \times 10^{13}) - \frac{58.5 \times 10^{2}}{2.303 \times 1.987 \times 800}$$

$= 13.1003 - 15.9799 = -2.8796$

$K = 1.3194 \times 10^{-3}\ \text{sec}^{-1}$

$$t_{1/2} = \frac{0.693}{1.3194} \times 10^{3}\ \text{sec} = 525\ \text{sec}$$

Problem 6: ***A carbon radio isotope $_ZX^A$ (half life 10 days) decays to give $_{Z-2}Y^{A-4}$. If 1.00 gm atom of $_ZX^A$ is kept in a sealed tube, how much helium will accumulate in 20 days ? Express the result in cm^3 at STP.***

Solution: Initial concentration (N_0) of radio-isotope is 1 gm atom. Concentration remained after 20 days may be calculated as

$$N_t = N_0\left(\frac{1}{2}\right)^n$$

where n = n_0 of half lives = 20/10 = 2 = $1\left(\frac{1}{2}\right)^2 = \frac{1}{4}$

Concentration decayed to α-particles = $1 - \frac{1}{4} = \frac{3}{4}$ gm atom. An α-particle takes 2 electron from air and from helium gas. Thus,

Helium formed $= \frac{3}{4}$ gm atom $= \frac{3}{4} \times 22400$ cc $= 16800$ cc

Problem 7: ***A radioactive isotope has an initial activity of 2×10^6 disintegration / min. After 4 days its activity is 9×10^5 dis/min. Find out the activity after 40 days.***

Solution: Initial activity $a_0 = 2\times10^6$ dpm

activity after 4 days $a_t = 9\times10^5$ dpm

$$K = \frac{2.303}{4}\log\frac{2\times10^6}{9\times10^5} = 0.19967 \text{ day}^{-1}$$

Activity after 40 days

$$0.19967 = \frac{2.303}{40}\log\frac{2\times10^6}{a_t}$$

$a_t = 699.31$ dpm

Problem 8: ***While studying the decomposition of $N_2O_5(g)$ it is observed that a plot of logarithm of its partial pressure versus time is linear. What kinetic parameter can be obtained from this.***

Solution: Consider 1st order

$$K_t = 2.303\log\frac{a}{a-x}$$

$K_t = 2.303\log a - 2.303\log(a-x)$ ..... (i)

In terms of pressure above equation (i) may by written as $a \propto P_0$

$(a - x) \propto P$

$K_t = 2.303\log P_0 - 2.303\log P$

$$\log P = -\frac{k}{2.303}t + \log P_0$$

Thus log P vs time graph is linear with intercept equal to $\log P_0$ and slope equal to $-\frac{k}{2.303}$. Since linear result are given thus decomposition in of 1st order.

Problem 9: ***From the following data for the reaction between A and B***

[A], mol lit^{-1}	***[B], mol lit^{-1}***	***Initial rate mol lit^{-1} s^{-1}, at***	
		300 K	***320 K***
2.5×10^{-4}	***3.0×10^{-5}***	***5.0×10^{-4}***	***2.0×10^{-3}***
5.0×10^{-4}	***6.0×10^{-5}***	***4.0×10^{-3}***	—
1.0×10^{-3}	***6.0×10^{-5}***	***1.6×10^{-2}***	—

Calculate the following

i) The order w.r.t. A and w.r.t. B
ii) The rate constant at 300 K
iii) The energy of activation
iv) The pre-exponential factor

Solution: (i) Rate = $K[A]^x[B]^y$

$5\times10^{-4} = K[2.5\times10^{-4}]^x[3\times10^{-5}]^y$ ....(1)

$4\times10^{-3} = K[5\times10^{-4}]^x[6\times10^{-5}]^y$ ....(2)

$1 \times 10^{-3} = K[1 \times 10^{-3}]\,[6 \times 10^{-5}]$ . . . .(3)

from equation (2) and (3)

order A, $x = 2$

form equation (1) and (2)

(ii) Rate constant at 30 K

Rate = $K[A]^2\,[B]$

$5 \times 10^{-4} = K[2.5 \times 10^{-4}]^2\,[3 \times 10^{-5}]$

$K = 2.667 \times 10^{8}$ mol^{-2} lt^{2} sec^{-1}

(iii) $\log \frac{K_2}{K_1} = \frac{Ea}{2.303}\left[\frac{1}{T_1} - \frac{1}{T_2}\right]$

$\log \frac{2 \times 10^{-3}}{5 \times 10^{-4}} = \frac{Ea}{2.303}\left[\frac{1}{300} - \frac{1}{32}\right]$

Ea = 55327 J mol^{-1}

(iv) $\log K = \log A - \frac{Ea}{2.303RT}$

$\log 5 \times 10^{-4} = \log A - \frac{55327}{2.303 \times 8.314 \times 300}$

$A = 1.143 \times 10^{18}$ mol^{2} sec^{-1}

Problem 10: ***In a pseudo first order hydrolysis of ester in water the following results were obtained:***

t/s	***0***	***30***	***60***	***90***
[ester]/M	***0.55***	***0.31***	***0.17***	***0.085***

i) Calculate the average rate of reaction between the time interval 30 to 60 seconds.

ii) Calculate the pseudo first order rate constant for the hydrolysis of ester.

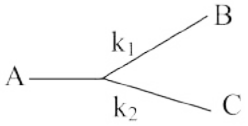
Solution: For hydrolysis of ester

$$K = \frac{2.303}{t}\log\frac{[Ester]_0}{[Ester]_t}$$

$K = \frac{2.303}{30}\log\frac{0.55}{0.31} = 1.92 \times 10^{-2}$ sec^{-1}

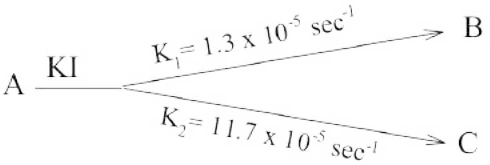
Also average rate = $\frac{0.31 - 0.17}{60 - 30} = 4.67 \times 10^{-3}$ mol lt^{-1} sec^{-1}

Problem 11: ***A certain organic compound A decomposes by two parallel first order mechanisms.***



If $K_1 : K_2 = 1:9$ and $k_1 = 1.3 \times 10^{-5}$ is^{-1}. Calculate the concentration ratio of C to A if an experiment is started with only A and allowed to run for one hour.

Solution:


A
KI
$K_1 = 1.3 \times 10^{-5}$ sec^{-1}
B
$K_2 = 11.7 \times 10^{-5}$ sec^{-1}
C

Rate constant (K_T) for decomposition of A = K_1 *K_2 = $(1.3 + 11.7) \times 10^{-5}$
= 13×10^{-5} moles of A decomposed into C in 1 hr. = mole of C formed in 1 hr.

so $K_2 = \frac{2.303}{3600} \log \frac{1}{1-x}$ (Let initial moles of A= 1)

$x = [C]_t = 0.3436$

Total moles of A remaining in 1 hr are calculated as

$$K_T = \frac{2.303}{3600} \log \frac{1}{[A]}$$

$[A]_t = 0.626$

so, $\frac{[C]_t}{[A]_t} = \frac{0.3436}{0.626} = 0.5486$

Problem 12: ***For a reaction: $A + B + C \rightarrow$ product,***
The rate of the reaction is given by
Rate = $K[A]^l[B]^m[C]^n$
From the following data determine
i) The order with respect to A
ii) The order with respect to B
iii) The order with respect to C
iv) The over all order
v) Rate constant

	Initial concentrations (mole dm^{-3})			***Initial rate (mole dm^{-3} s^{-1})***
	[A]	***[B]***	***[C]***	
a)	***0.010***	***0.005***	***0.010***	***5.0×10^{-5}***
b)	***0.010***	***0.005***	***0.015***	***5.0×10^{-5}***
c)	***0.010***	***0.010***	***0.010***	***2.5×10^{-5}***
d)	***0.020***	***0.005***	***0.010***	***14×10^{-5}***

Solution: Rate = $K[A]^l\,[B]^m\,[C]^n$

$[0.01]^l\,[0.005]^m\,[0.01]^n = 5 \times 10^{-5}$ . . . . . (1)
$[0.01]^l\,[0.005]^m\,[0.015]^n = 5 \times 10^{-5}$ . . . . . (2)
$[0.01]^l\,[0.01]^m\,[0.01]^n = 2.5 \times 10^{-5}$ . . . . . (3)

$[0.02]^l\,[0.005]^m\,[0.01]^n = 14 \times 10^{-5}$ . . . . . (4)

from equation (1) and (4)

order w.r.t [A] = 2/3

from equation (1) and (2)

order w.r.t. [B] = -1

from equation (1) and (2)

order w.r.t [C] = 0

overall order = $\left(\frac{3}{2}\right) - 1 + 0 = \frac{1}{2}$

Rate const. (K) is calculated as

$5 \times 10^{-5} = K\,[0.01]^{3/2}\,[0.005]^{-1}\,[0.01]^{0}$

$K = 2.5 \times 10^{-4}$ $(\text{mol dm}^{-3})^{1/2}\,\text{sec}^{-1}$

Problem 13: ***A drug is known to be ineffective after it has decomposed to the extent of 30%. The original concentration of a sample was 500 units/ml. When analysed 20 months later, the concentration was found to be 420 units / ml. Assuming that the decomposition is of first order, what will be the expiration time of the drug sample. What is the half life of the drug.***

Solution: First calculate the value of K

$$K = \frac{2.303}{20}\log\frac{500}{420}$$

$K = 8.72 \times 10^{-3}$ month^{-1}

drug will be ineffective when decomposed to 30%

$$K = \frac{2.303}{t}\log\frac{100}{70}$$

$$t = \frac{2.303}{8.72 \times 10^{-3}}\log\frac{100}{70} = 40.9 \text{ months}$$

$$t_{1/2} = \frac{0.693}{8.72 \times 10^{-3}} = 79.49 \text{ months}$$

Problem 14: ***The decomposition of formic acid on a gold surface follows first order kinetics and specific rate constants are 5.5 × 10^{-4} s^{-1} and 9.2 × 10^{-3} s^{-1} at 140°C and 185°C respectively. Calculate energy of activation.***

Solution: Follow the equation

$$\log\frac{K_2}{K_1} = \frac{Ea}{2.303R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right]$$

$$\log\frac{9.2 \times 10^{-3}}{5.5 \times 10^{-4}} = \frac{Ea}{2.303 \times 8.314}\left[\frac{1}{413} - \frac{1}{458}\right]$$

$Ea = 9.916 \times 10^{4}$ J/mole

$Ea = 2.37 \times 10^{4}$ J/mole

Problem 15: ***Two reactions proceed at 25°C at the same rate, the temperature coefficient of the rate of the first reaction is 2.0 and of the second, 2.5. Find the ratio of rates of these reactions at 95°C.***

Solution:

	rx_n (I)	rx_n (II)
at 25^0C	r	r
$35\ ^0C$	2r	2.5 r
$45\ ^0C$	$(2)^2r$	$(2.5)^2\ r$
$55\ ^0C$	$(2)^3r$	$(2.5)^3\ r$
$65\ ^0C$	$(2)^4r$	$(2.5)^4\ r$
$75\ ^0C$	$(2)^5r$	$(2.5)^5\ r$
$85\ ^0C$	$(2)^6r$	$(2.5)^6\ r$
$95\ ^0C$	$(2)^7r$	$(2.5)^7\ r$

$$\text{ratio of rates} = \frac{rate\ of\ reaction(ii)}{rate\ of\ reaction(i)} = \frac{(2.5)^7\ r}{(2)^7\ r} = 4.77\ times$$

$$= 5 \text{ times}$$

Assignments (New Pattern)

SECTION – I   Single Choice Questions

LEVEL - I

1. For a hypothetical reaction : $A + B \rightarrow$ Product, the rate law is
$r = k [B] [A]^0$, the order of reaction is
(a) 0
(b) 1
(c) 2
(d) 3.

2. A hypothetical reaction $A_2 + B_2 \rightarrow 2AB$ follows the mechanism as given below:
$A_2 \rightarrow A + A$ (fast)
$A + B_2 \rightarrow AB + B$ (slow)
$A + B \rightarrow AB$ (fast)
The order of the overall reaction is
(a) 2
(b) 1
(c) $1\frac{1}{2}$
(d) 0.

3. 99% of a first order reaction was completed in 32 min. When will 99.9% of the reaction complete ?
(a) 24 min
(b) 8 min
(c) 4 min
(d) 48 min

4. A gaseous reaction: $A_2(g) \rightarrow B(g) + \frac{1}{2} C(g)$. Shows increase in pressure from 100 mm to 120 mm in 5 minutes. The rate of disappearance of A_2 is
(a) 4 mm min^{-1}
(b) 8 mm min^{-1}
(c) 16 mm min^{-1}
(d) 2 mm min^{-1}.

5. The half life period for catalytic decomposition of AB_3 at 50 mm in found to be 4 hrs and at 100 mm it is 2.0 hrs. The order of reaction is
(a) 3
(b) 1
(c) 2
(d) 0

6. For a reaction : $X(g) \rightarrow Y(g) + Z(g)$
The half-life period is 10 min. In what period of time would be concentration of X be reduced to 10% of original concentration ?
(a) 20 min.
(b) 33 min
(c) 15 min
(d) 25 min.

7. The rate of the reaction $A + B_2 \longrightarrow AB + B$ is directly proportional to the concentration of A and independent of concentration of B_2, hence, rate law is:

(a) $k[A][B_2]$ (b) $k[A]^2[B_2]$
(c) $k[A]$ (d) $k[B_2]$

8. $A \rightarrow$ Product, $[A]_0 =$ 2M. After 10 minutes reaction is 10% completed. If $-\frac{d[A]}{dt} = k[A]$ then T_{50} is approximately:

(a) 0.693 min (b) 69.3 min
(c) 66.0 min (d) 0.0693 min

9. The rate constant for the reaction
$2N_2O_5 \longrightarrow 4NO_2 + O_2$
is $3 \times 10^{-5} s^{-1}$. If the rate at a given time is 2.40×10^{-5} mol L^{-1} s^{-1}, then concentration of N_2O_5 at that time is:

(a) 1.4 (b) 1.2
(c) 0.04 (d) 0.8

10. Calculate the half-life of the first-order reaction
$C_2H_4O(g) \rightarrow CH_4(g) + CO(g)$
if the initial pressure of $C_2H_4O(g)$ is 80 mm and the total pressure at the end of 20 minutes is 120 mm.

(a) 40 min (b) 120 min
(c) 20 min (d) 80 min

11. Rate constant of a first order reaction is 0.0693 min^{-1}. If we start with 20 mol L^{-1}, it is reduced to 2.5 mol L^{-1} in:

(a) 10 min (b) 20 min
(c) 30 min (d) 40 min

12. In the first order reaction the concentration of reactant decreases from 2 M to 0.50 M in 20 minutes. The value of specific rate is

(a) 69.32 (b) 6.932
(c) 0.6932 (d) 0.06932

13. Rate of the chemical reaction : $nA \rightarrow$ products, is doubled when the concentration of A is increased four times. If the half time of the reaction at any temperature is 16 min. then time required for 75% of the reaction to complete is

(a) 24.0 min. (b) 27.3 min.
(c) 48 min. (d) 49.4 min.

14. For a first order reaction the ratio of $t_{0.75}$ to $t_{0.50}$ would be

(a) 4 : 3 (b) 3 : 2
(c) 2 : 1 (d) 1 : 2

15. Two substances A($t_{1/2}$ = 5 min.) and B($t_{1/2}$ = 15 min.) are taken in such away that initially $[A]_0 = 4[B]_0$. The time after which both the concentrations will be equal is
(a) 5 min.
(b) 15 min.
(c) 20 min
(d) Concentrations can never be equal

16. Two substances A($t_{1/2}$ = 5 min.) and B($t_{1/2}$ = 15 min.) are taken in such away that initially [A] = 4[B]. The time after which both the concentrations will be equal is
(a) 5 min.
(b) 15 min.
(c) 20 min.
(d) concentrations can never be equal

17. The time elapsed of a certain reaction between 33% and 67 % completion of a first order reaction is 30 minutes. What is the time needed for 25% completion?
(a) 150.5 minutes
(b) 125 minutes
(c) 180.5 minutes
(d) 165.5 minutes

18. The rate constant of a reaction is 6.93×10^{-3} min^{-1}. If initial concentration of the reactant is 2.0 M, the rate after 100 minutes
(a) 6.93×10^{-3} mol L^{-1} min^{-1}
(b) 6.93×10^{-5} mol L^{-1} min^{-1}
(c) $6.93 \times 10^{-3} \times 2$ mol L^{-1} min^{-1}
(d) $6.93 \times 10^{-3} \times 0.5$ mol L^{-1} min^{-1}

19. For the first order reaction $C_2H_4O_{(g)} \rightarrow CH_{4(g)} + CO_{(g)}$, the initial pressure of $C_2H_4O(g)$ is 80 torr and total pressure at the end of 20 minutes is 120 torr. The time needed for 75% decomposition of C_2H_4O would be
(a) 20 minutes
(b) 40 minutes
(c) 80 minutes
(d) 120 minues

20. The rate constant of a reaction at 27°C is 2.3×10^{-3} min^{-1} and at this temperature 0.001 % of the reactant molecules are able to cross over the energy barrier existing between the reactants and the products. What can the maximum value of rate constant be achieved on raising the temperature ?
(a) 23.0 min^{-1}
(b) 2.3×10^{-2}
(c) 115.0 min^{-1}
(d) 230.0 min^{-1}

LEVEL – II

1. In the formation of sulphur trioxide by the contact process.
$2SO_{2(g)} + O_{2(g)} \rightleftharpoons 2SO_{3(g)}$
The rate of reaction is expressed as
$$-\frac{d(O_2)}{dt} = 2.5 \times 10^{-4} \text{ mole}^{-1}\text{L}^{-1}\text{ sec}^{-1}$$
The rate of disappearance of (SO_2) will be
(a) 5.0×10^{-4} mol L–1 s^{-1}
(b) -2.25×10^{4} mol L^{-1} s^{-1}
(c) 3.75×10^{-4} mol L^{-1} s^{-1}
(d) 50.0×10^{-4} mol L^{-1} s^{-1}.

2. For the reaction $2NH_3 \longrightarrow N_2 + 3H_2$

$$-\frac{d[NH_3]}{dt} = k_1[NH_3],\ \frac{d[N_2]}{dt} = k_2[NH_3],\ \frac{d[H_2]}{dt} = K_2[NH_3]$$

Then relation between k_1, k_2 and k_3 is:

(a) $1.5k_1 = 3k_2 = k_3$	(b) $2k_1 = k_2 = 3k_2$
(c) $k_1 = k_2 = k_3$	(d) $k_1 = 3k_2 = 2k_3$

3. The decomposition of nitrogen pentoxide can be represented as

$N_2O_5(g) \rightarrow 2NO_2(g) + \frac{1}{2}O_2(g)$

The rate of the reaction can be expressed as

(a) $-\frac{d[N_2O_5]}{dt} = 2\frac{d[NO_2]}{dt} = \frac{1}{2}\frac{d[O_2]}{dt} = k[N_2O_5]$

(b) $\frac{1}{2}\frac{d[N_2O_5]}{dt} = \frac{1}{2}\frac{d[NO_2]}{dt} = \frac{d[O_2]}{dt} = k[N_2O_5]$

(c) $-\frac{d[N_2O_5]}{dt} = \frac{1}{2}\frac{d[NO_2]}{dt} = 2\frac{d[O_2]}{dt} = k[N_2O_5]$

(d) $-\frac{d[N_2O_5]}{dt} = \frac{1}{2}\frac{d[NO_2]}{dt} = \frac{1}{2}\frac{d[O_2]}{dt} = k[N_2O_5]$

4. Rate of formation of SO_3 in the following reaction

$2SO_2 + O_2 \longrightarrow 2SO_3$

is 100 g min^{-1}. Hence, rate of disappearance of O_2 is:

(a) 50 g min^{-1}	(b) 100 g min^{-1}
(c) 200 g min^{-1}	(d) 40g min^{-1}

5. For a chemical reaction A → B, the rate of reaction increases by a factor of 1.837 when the concentration of A is increased by 1.5 times. The order of reaction with respect to A is

(a) 1	(b) 1.5
(c) 2	(d) –1

6. In which of the following case, E_a of the backward reaction is greater than that of the forward reaction?

(a) $A + 10\text{ kcal} \longrightarrow B$, $E_a = 50$ kcal	(b) $A + 20\text{ kcal} \longrightarrow B$, $E_a = 40$ kcal
(c) $A + 40\text{ kcal} \longrightarrow B$, $E_a = 10$ kcal	(d) $A - 40\text{ kcal} \longrightarrow B$, $E_a = 20$ kcal

7. $\underset{(g)}{A} \longrightarrow \underset{(g)}{B} + \underset{(g)}{C}$

$\frac{-d[A]}{dt} = k[A]$

At the start pressure is 100 mm and after 10 min, pressure is 120 mm. Hence rate constant (min^{-1}) is:

(a) $\frac{2.303}{10}\log\frac{120}{100}$	(b) $\frac{2.303}{10}\log\frac{100}{20}$
(c) $\frac{2.303}{10}\log\frac{100}{80}$	(d) $\frac{2.303}{10}\log\frac{100}{120}$

8. The reaction : $A(g) + 2B(g) \longrightarrow C(g) + D(g)$
Initial pressure of A and B are respectively $p_A = 0.60$ atm, $p_B = 0.80$ atm. when $p_C = 0.20$ atm, the rate of the reaction, relative to the initial rate, is:
(a) $\frac{1}{48}$ (b) $\frac{1}{24}$
(c) $\frac{1}{6}$ (d) $\frac{1}{4}$

9. The rate law for the dimerisation of NO_2 is $\frac{-d[NO_2]}{dt} = k[NO_2]^2$
Which of the following changes will change the value of the specific rate constant, k:
(a) doubling the total pressure on the system (b) doubling the temperature
(c) both (d) none of these

10. For a reaction for which the activation energies of the forward and reverse directions are equal in value:
(a) the stoichiometry is the mechanism (b) $\Delta H = 0$
(c) $\Delta S = 0$ (d) the order is zero

SECTION – II **May be more than one choice**

1. Which of the following statements are correct?
(a) The order of a reaction is the sum of the components of all the concentration terms in the rate equation.
(b) The order of a reaction with respect to one reactant is the ratio of the change of logarithm of the rate of the reaction to the change in the logarithm of the concentration of the particular reactant, keeping the concentrations of all other reactants constant.
(c) Orders of reactions can be whole numbers of fractional numbers.
(d) The order of a reaction can only be determined from the stoichiometric equation for the reaction.

2. Which of the following statements are correct?
(a) The rate of the reaction involving the conversion of ortho-hydrogen to parahydrogen is $-\frac{d[H_2]}{dt} = k[H_2]^{3/2}$
(b) The rate of the reaction involving the thermal decomposition of acetaldehyde is $k[CH_3CHO]^{3/2}$
(c) In the formation of phosgene gas from CO and Cl_2, the rate of the reaction is $k[CO][Cl_2]^{1/2}$
(d) In the decomposition of H_2O_2, the rate of the reaction is $k[H_2O_2]$

3. Which of the following reactions is of the first order?
(a) The decomposition of ammonium nitrate in an aqueous solution

(b) The inversion of cane-sugar in the presence of an acid
(c) The acidic hydrolysis of ethyl acetate
(d) All radioactive decays

4. The calculation of the pre-exponential factor is based on the
(a) idea that, for a reaction to take place, the reactant species must come together
(b) calculation of the molecularity of the reaction
(c) idea that the reactant species must come together, leading to the formation of the transition state which then transforms into the products
(d) calculation of the order of the reaction

5. The basic theory behind Arrhenius's equation is that
(a) the number of effective collisions is proportional to the number of molecules above a certain threshold energy
(b) as the temperature increases, so does the number of molecules with energies exceeding the threshold energy
(c) the rate constant is a function of temperature
(d) the activation energy and pre-exponential factor are always temperature-independent

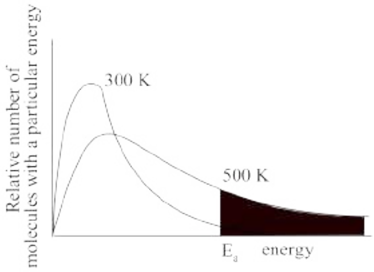
6. In Arrhenius's equation, $k = A \exp\left(-\frac{E_a}{RT}\right)$. A may be termed as the rate constant at
(a) very low temperature
(b) very high temperature
(c) zero activation energy
(d) the boiling temperature of the reaction mixture

7. Rate constant k varies with temperature by eqn:
$\log k\ (\text{min}^{-1}) = 5 - \frac{2000\ \text{K}}{T}$. We can conclude
(a) pre-exponential factor A is 5
(b) E_a is 2000 kcal
(c) pre-exponential factor A is 10^5
(d) E_a is 9.212 kcal

8. A reaction is catalysed by H^+ ion. In presence of HA, rate constant is 2×10^{-3} min^{-1} and in presence of HB rate constant is 1×10^{-3} min^{-1}, HA and HB both being strong acids, we may conclude:
(a) equilibrium constant is 2
(b) HAis stronger than HB
(c) relative strength of HA and HB is 2
(d) HA is weaker than HB and relative strength is 0.5

9. Which of the following statements are correct?
(a) A plot of log K_p versus 1/T is linear
(b) A plot of log [X] versus time is linear for a first order reaction $X \longrightarrow P$
(c) A plot of log P versus 1/T is linear at constant volume
(d) A plot of P versus 1/V is linear at constant temperature

10. The distribution of molecular kinetic energy at two temperatures is as shown in the following graph.



Which of the following conclusions are correct?

(a) The number of molecules with energy E_a or greater is proportional to the shaded area for each temperature

(b) The number of molecules with energy E_a or less is proportional to the shaded area for each temperature.

(c) The number of molecules with energy E_a is the mean of all temperatures

(d) The graph follows the Maxwell-Boltzmann energy distribution law.

SECTION – III Other Engg. Exam Questions

1. For the reaction $2N_2O_5 \rightarrow 4NO_2 + O_2$ rate of reaction and rate constant are 1.02×10^{-4} and 3.4×10^{-5} sec^{-1} respectively. The concentration of N_2O_5 at that time will be
(a) 1.732
(b) 3
(c) 1.02×10^{-4}
(d) 3.4×10^{5}

2. A reaction involving two different reactants
(a) Can never be a second order reaction
(b) Can never be a unimolecular reaction
(c) Can never be a bimolecular reaction
(d) Can never be a first order reaction

3. What is the order of a reaction which has a rate expression rate = $K[A]^{3/2}[B]^{-1}$
(a) 3/2
(b) 1/2
(c) 0
(d) none of these

4. Which of the following expression is correct for first order reaction ? (CO) refers to initial concentration of reactant
(a) $t_{1/2} \propto CO$
(b) $t_{1/2} \propto CO^{-1}$
(c) $t_{1/2} \propto CO^{-2}$
(d) $t_{1/2} \propto CO^{0}$

5. Which of the following statements about zero order reaction is not true
(a) Its unit is sec^{-1}
(b) The graph between log (reactant) versus rate of reaction is a straight line
(c) The rate of reaction increases with the increase in concentration of reactants
(d) Rate of reaction is independent of concentration of reactants

6. For the reaction $A + 2B \rightarrow C$, rate is given by $R = [A][B]^2$ then the order of the reaction is

(a) 3	(b) 6
(c) 5	(d) 7

7. Units of rate constant of first and zero order reactions in terms of molarity M unit are respectively

(a) sec^{-1}, M sec^{-1}	(b) sec^{-1}, M
(c) M sec^{-1}, sec^{-1}	(d) M, sec^{-1}

8. For the reaction system $2NO (g) + O_2 (g) \rightarrow 2NO_2 (g)$ volume is suddenly reduced to half its value by increasing the pressure on it. If the reaction is of first with respect to O_2 and second order with respect to NO, the rate of reaction will
(a) Diminish to one fourth of its initial value
(b) Diminish to one eighth of its initial value
(c) Increase to eight times of its initial value
(d) Increase to four times of its initial value

9. In the first order reaction, the concentration of the reactant is reduced to 25% in one hour. The half life period of the reaction is

(a) 2hr	(b) 4hr
(c) 1/2 hr	(d) 1/4 hr

10. For a reaction, $X (g) \rightarrow Y(g) + Z(g)$ the half life period is 10 min. In what period of time would the concentration of X be reduced to 10% of original concentration

(a) 20 min	(b) 33 min
(c) 15 min	(d) 25 min

11. A radioactive isotope having a half-life of 3 days was received after 12 days. It was found that there were 3 gm of the isotope in the container. The initial weight of the isotope when packed was

(a) 12 gm	(b) 24 gm
(c) 36 gm	(d) 48 gm

12. Half-life period of a first order reaction is
(a) Inversely proportional to the concentration
(b) Independent of the concentration
(c) Directly proportional to the initial concentration
(d) Directly proportional to the final concentration

13. A radioactive element resembling iodine in properties is

(a) Astatine	(b) Lead
(c) Radium	(d) Thorium

14. The C^{14} to C^{12} ratio in a wooden article is 13% that of the fresh wood. Calculate the age of the wooden article. Given that the half-life of C^{14} is 5770 yers.

(a) 16989 years (b) 16858 years
(c) 15675 years (d) 17700 years

15. Hydrogen bomb is based on the principle of
(a) Nuclear fission (b) Natural radioactivity
(c) Nuclear fusion (d) Artificial radioactivity

SECTION – IV **Comprehension Type Questions**

✍ **Write-up I**

Arrhenius studied the effect of temperature on the rate of a reaction and postulated that rate constant varies with temperature exponentially as k = $Ae^{-E_a/RT}$. For most of the reactions, it was found that the temperature coefficient of the reaction lies between 2 to 3. The method is generally used for finding the activation energy of a reaction. Keeping temperature constant, the effect of catalyst on the activation energy has also been studied by studying how much the rate of reaction changes in the presence of catalyst. In most of the cases, it is observed that catalyst lowers the activation energy barrier and increases the rate of reaction.

1. The pre-exponential factor in the Arrhenus equation of a second order reaction has the units
(a) mol L^{-1} s^{-1} (b) L mol^{-1} s^{-1}
(c) s^{-1} (d) dimensionless

2. If the rate of reaction grows 15.6 times on increasing the temperature by 30 K, the temperature coefficient of the reaction will be nearly
(a) 2 (b) 2.5
(c) 3.0 (d) 3.5

3. If ‘x’ is the fraction of molecules having energy greater than E_a, it will be given by
(a) $x = -\frac{E_a}{RT}$ (b) $\ln x = -\frac{E_a}{RT}$
(c) $x = e^{E_a/RT}$ (d) None of these

✍ **Write-up II**

Rate of forward reaction decreases and that of backward reaction increases with passage of time. The rate of reaction increases considerable with an increase in temperature.

4. The rate of a chemical reaction generally increases rapidly even for small temperature increase because of rapid increase in the
(a) collision frequency (b) fraction of molecules
(c) activaton energy (d) average kinetic energy of molecules

5. The temperature coefficient of a reaction is:
(a) ratio of rate constants at two temperatures differing by 1°C

(b) ratio of rate constants at temperature 35°C and 25°C
(c) ratio of rate constants at temperature 30°C and 25°C
(d) specific reaction rate at 25°

6. The specific rate constant of a first order reaction depends on
(a) concentration of the reactants (b) concentration of products
(c) times (d) temperature

✍ **Write-up III**

The rate law for the decomposition of gaseous N_2O_5 is $N_2O_5 \longrightarrow 2NO_2 + \frac{1}{2}O_2$. A reaction mechanism which has been suggested

$N_2O_5 \xrightleftharpoons{K_{eq}} NO_2 + NO_3$ (fast equilibrium)

$NO_2 + NO_3 \xrightarrow{K_1} NO_2 + NO + O_2$ (slow)

$NO + NO_3 \xrightarrow{K_2} 2NO_2$ (fast)

7. In 20 minutes of 80% of N_2O_5 is decomposed find rate constant
(a) 0.08 (b) 0.05
(c) 0.12 (d) 0.2

8. At the equilibrium state N_2O_5, NO_2 and NO_3 concentrations are 0.2, 0.4 and 0.4 M respectively. Find K_1
(a) 0.1 (b) 0.2
(c) 1 (d) 2

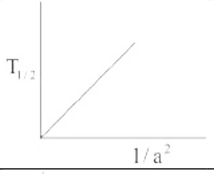
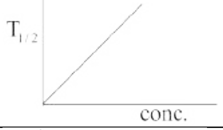
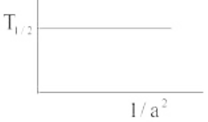
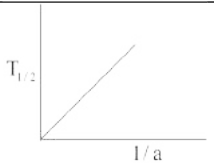
9. When graph is plotted between $t_{1/2}$ V_s initial concentration then slope is
(a) 0 (b) ∞
(c) >0 (d) <0

SECTION – V **Match the column**

1. Match column – I with column – II and select the correct answer using the codes given below the lists.

Column - I		Column - II	
(A)	Collision theory	(p).	Mol $L^{-1}s^{-1}$
(B)	Zero order reaction	(q)	Bimolecular reaction
(C)	Photochemical reaction	(r)	Fractional
(D)	Intercept (in Arrhenius plot)	(s)	In A
(E)	Order of reaction	(t)	Zero order reaction

2. Match column – I with column – II.

	Column – I (order of reaction)		Column – II (plots of $T_{1/2}$ vs conc.)
(A)	zero	(p)	
(B)	First	(q)	
(C)	Second	(r)	
(D)	Third	(s)	

SECTION – IV Subjective Questions

LEVEL – I

1. Radioactive decay is a first order process. Radioactive carbon wood sample decays with a half life of 5770 years. What is the rate constant in $(\text{years})^{-1}$ for the decay? What fraction would remain after 11540 years?

2. The inactivation of a viral preparation in a chemical bath is found to be a first order reaction (a) calculate the rate constant for the viral inactivation if in the beginning 1.5 % of the virus is inactivated per minute. Also calculate the time required for (b) 50% inactivation and (c) 80% inactivation of the virus.

3. The first order reaction has $k = 1.5 \times 10^6$ per second at 200°C. If the reaction is allowed to run for 10 hours, what percentage of the initial concentration would have changed in the product? What is the half-life period of this reaction?

4. Substance A reacts according to first order rate law with $k = 5.0 \times 10^{-5}\ s^{-1}$.
   a) If the initial concentration of A is 1.0 M what is the initial rate?
   b) What is the rate after 1.0 hour.

5. The decomposition of Cl_2O_7 at 440K in the gas phase to Cl_2 and O_2 is a first order reaction.

i) After 55 seconds at 400 K the pressure of Cl_2O_7 falls from 0.062 to 0.044 atm., calculate that rate constant.
ii) Calculate the pressure of Cl_2O_7 after 100 sec. of decomposition at this temperature.

6. For the reaction $2NO + Cl_2 \longrightarrow 2NOCl$, it was found that on doubling concentration of both reactants the rate increases eight fold. But on doubling the concentration of chlorine alone, rate only doubles. What is the overall order.

7. For the reaction:
$2A + B + C \rightarrow A_2B + C$
the rate = $k[A][B]^2$ with $k = 2 \times 10^{-6}\ M^{-2}s^{-1}$. Calculate the initial rate of the reaction when [A] = 0.1 M, [B] = 0.2 M and [C] = 0.8 M. If the rate of reverse reaction is negligible then calculate the rate of reaction after [A] is reduced to 0.06 M.

8. Rate law for the following reaction; is
Ester + $H^+ \rightleftharpoons$ Acid + Alcohol; is
$\frac{dx}{dt} = K\,[\text{ester}]^1\,[H^+]^0$
What would be the effect on the rate if
i) Concentration of ester is doubled ?
ii) Concentration of H+ ion is doubled ?

9. Calculate the half life of a first order reaction from their rate constants given below:
a) 200 s^{-1}; b) 2 min^{-1}; c) 4 $year^{-1}$

10. The rate constant for a first order reaction is 60 s^{-1}. How much time will it take to reduce the initial concentration of the reactant to its 1/16th value?

LEVEL – II

1. A sample of $_{53}I^{131}$, as iodide ion, was administered to a patient in a carrier consisting of 0.10 mg of stable iodide ion. After 4.00 days, 67.7% of the initial radioactivity was detected in the thyroid gland of the patient. What mass of the stable iodide ion had migrated to the thyroid gland? Given $T_{1/2}$ I^{131} = 8 days.

2*. $_{84}Po^{210}$ decays with α particle to $_{82}Pb^{206}$ with a half life of 138.4 days. If 1.0 g of $_{84}Po^{210}$ is placed in a sealed tube, how much helium will accumulate in
69.2 days. Express the answer in cm^3 at STP.

3*. At 380°C, the half-life period for the first order decomposition of H_2O_2 is 360 min. the energy of activation of the reaction is 200 kJ mol^{-1}, Calculate the time required for 75% decomposition at 450°C.

4. The rate constant of a reaction is $1.5 \times 10^7\ s^{-1}$ at 50°C and $4.5 \times 10^7\ s^{-1}$ at 100°C. Evaluate the Arrhenius parameters A and E_a.

5*. 5 ml of ethylacetate was added to a flask containing 100 ml of 0.1 N HCl placed in a thermostat maintained at 30°C. 5 ml of the reaction mixture was withdrawn at different intervals of time and after chilling, titrated against a standard alkali. The following data were obtained :

Time (minutes)	0	75	119	183	∞
ml of alkali used	9.62	12.1	13.10	14.75	21.05

Show that hydrolysis of ethyl acetate is a first order reaction.

6. In presence of an acid N-chloro acetanilide changes slowly into p-chloro acetanilide. Former substance liberated iodine from KI and not the later and hence progress of reaction can be measured by titrating iodine liberated with $Na_2S_2O_3$ solution, the results obtained were as follows :

Time (hours)	0	1	2	4	6	8
(a–x)i.e., hypo	45	32	22.5	11.3	3.7	2.9

show that reaction is uniomlecular and find out the fraction of N-chloroacetanilide decomposed after three hours.

7. For the reaction
$2NO(g) + H_2(g) \rightarrow N_2O(g) + H_2O(g)$ at 900 K, the following data are obtained :

Initial pressure of NO (atm)	Initial pressure of H_2(atm)	Rate (atm min^{-1})
0.150	0.400	0.020
0.075	0.400	0.005
0.150	0.200	0.010

Find the rate law and the value of rate constant.

8. Bicyclohexane was found to undergo two parallel first order rearrangements. At 730 K, the first order rate constant for the formation of cyclohexane was measured as 1.26×10^{4} s^{1}, and for the formation of methyl cyclopentene the rate constant was 3.8×10^{5} s^{1}. What is the percentage distribution of the rearrangement products ?

9*. 10 gram atoms of an α-active radio isotope are disintegrating in a sealed container. In one hour the helium gas collected at STP is 11.2 cm^3. Calculate the half-life of the radio-isotope.

10. Decomposition of diazobenzene chloride was followed at constant temperature by measuring the volume of nitrogen evolved at suitable intervals. Following readings were observed.

Time	0	20	55	70	∞
Vol. of N_2	0	10	25	33	162

Calculate order of the reaction.

LEVEL – III (Judge yourself at JEE level)

1*. 1 g atm of Ra^{226} is place in an evacuated tube of volume 5 litre. Assuming that each $_{88}Ra^{226}$ nucleus is an α-emitter and all the contents are present in tube, calculate the total pressure of gases and partial pressure of He collected in tube at 27°C after the end of 800 years. $t_{1/2}$ of Ra is 1600 year. Neglect volume occupied by undecayed Ra.

2. A solution contains 1 milli-curier of L-phenyl alanine C^{14} (uniformly labeled) in 2.0 mL solution. The activity of labeled sample is given as 150 milli-curie/milli-mole. Calculate:
   a) The concentration of sample in the solution in mole/litre.
   b) The activity of the solution in terms of counting per minute/mL at a counting efficiently of 80%.

3*. Two reactions (I) A $\rightarrow$ Products (II) B $\rightarrow$ Products follow first order kinetics. The rate of the reaction (I) is doubled when temperature is raised from 300K to 310K. The half life for this reaction at 310 K is 30 minute. At the same temperature B decomposes twice as fast as A. If the energy of activation for the reaction (II) is half that of reaction (I), calculate the rate constant of reaction (II) at 300K.

4. A solution contains a mixture of isotopes of X^{A_1} ($t_{1/2}$ = 14 days) and X^{A_2} ($t_{1/2}$ = 25 days). Total activity is 1 curie at t = 0. The activity reduces by 50% in 20 days. Find :
   a) The initial activities of X^{A_1} and X^{A_2}.
   b) The ratio of their initial no. of nuclei.

5. The rate of decomposition for methyl nitrite and ethyl nitrite can be given in terms of rate constant (in sec^{-1}) K_1 and K_2 respectively. The energy of activations for the two reactions are 152.30 kJ mol^{-1} and 157.7 kJ mol^{-1} as well as frequency factors are 10^{13} and 10^{14} respectively for the decomposition of methyl and ethyl nitrite. Calculate the temperature at which rate constant will be same for the two reactions.

6*. A given sample of milk turns sour at room temperature (20°C) in 64 hours. In a refrigerator at 3°C, milk can be stored three times as long before it sours. Estimate
   a) The activation energy for souring of milk,
   b) How long it take milk to sour at 40°C ?

7. A 22.4 litre flask contains 0.76 mm of ozone at 25°C. Calculate:
   i) the concentration of oxygen atoms needed so that the reaction $O + O_3 \rightarrow 2O_2$ having rate constant equal to 1.5×10^7 litre mol^{-1} sec^{-1} can proceed with a rate of 0.15 mol $litre^{-1}$ sec^{-1}.
   ii) the rate of formation of oxygen under this condition.

8*. Decomposition of H_2O_2 is a first order reaction. A solution of H_2O_2 labelled as 20 volumes was left open. due to this some H_2O_2 decomposed. To determine the new volume strength after 6 hours, 10 mL of this solution was diluted to 100 mL 10 mL of this diluted solution was titrated against 25 mL of 0.025 M $KMnO_4$ acidified solution. Calculate the rate constant for decomposition of H_2O_2.

9. $^{238}_{92}U$ is radioactive and it emits α and β particles to form $^{206}_{82}Pb$. Calculate the number of α and β particles emitted in this conversion. An ore of $^{238}_{92}U$ is found to contain $^{238}{}_{92}U$ and $^{206}_{82}Pb$ in the weight ratio of 1:0.1. The half-life period of $^{238}_{92}U$ is 4.5×10^9 years. Calculate the age of the ore.

10*. ^{64}Cu (half-life = 12.8h) decays by β^- emission (38%), β^+ emission (19%) and electron capture (43%). Write the decay products and calculate partial half-lives for each of the decay processes.

Answers to Assignments

SECTION - I

LEVEL - I

1.	**(b)**	**2.**	**(c)**	**3.**	**(d)**	**4.**	**(b)**
5.	**(c)**	**6.**	**(b)**	**7.**	**(c)**	**8.**	**(c)**
9.	**(d)**	**10.**	**(c)**	**11.**	**(c)**	**12.**	**(d)**
13.	**(b)**	**14.**	**(c)**	**15.**	**(b)**	**16.**	**(b)**
17.	**(b)**	**18.**	**(a)**	**19.**	**(b)**	**20.**	**(d)**

LEVEL - II

1.	**(a)**	**2.**	**(a)**	**3.**	**(d)**	**4.**	**(d)**
5.	**(b)**	**6.**	**(d)**	**7.**	**(c)**	**8.**	**(c)**
9.	**(b)**	**10.**	**(b)**				

SECTION - II

1.	**(a, b, c)**	**2.**	**(a, b, c, d)**	**3.**	**(a, b, c, d)**
4.	**(a, c)**	**5.**	**(a, b, c)**	**6.**	**(b, c)**
7.	**(c, d)**	**8.**	**(b, c)**	**9.**	**(a), (b), (d)**
10.	**(a, d)**				

SECTION - III

1.	**(b)**	**2.**	**(b)**	**3.**	**(b)**	**4.**	**(b)**
5.	**(d)**	**6.**	**(b)**	**7.**	**(a)**	**8.**	**(a)**
9.	**(c)**						

SECTION - IV

1. **(a - q), (b – p), (c - t), (d - s), (e – r)**

2. **(a - q), (b – r), (c – s), (d – p)**

SECTION - V

LEVEL – I

1. $\frac{1}{4.002}$

2. (a) 2.5×10^{-4} s^{-1} (b) 46 min (c) 10.7 min

3. $t_{1/2} = 128.33$ hr.

4. (a) 5.0×10^{-5} mol S^{-1}; (b) 4.117×10^{-5} S^{-1}

5. (i) 6.236×10^{-3} s^{-1} ; (ii) 0.0332 atm

6. 3

7. i) 8.0×10^{-9} M^{-2} s^{-1}; (ii) 3.89×10^{-9} M^{-2} s^{-1}

8. i) rate is doubled ; ii) rate is unaffected

9. a) 3.47×10^{-3} seconds; (b) 0.35 minutes; (c) 0.173 years

10. 4.6×10^{-2} seconds

LEVEL – II

1. 0.09575 mg

2. 31.25 cm^3

3. 20.33 min

4. $E_a = 2.2 \times 10^4$ J mol^{-1}

   $A = 5.4 \times 10^{10}$

6. 0.658

7. $r = [P_{NO}]^2 [P_{H2}]$

   $K = 2.22$ atm^{-2} min^{-1}

8. 23%.

9. 1.58 years

10. First

LEVEL – III

1. 2.887 atm, 1.443 atm

4. (a) 0.3669 Ci, 0.6331 Ci (b) 0.3245

7. (i) 2.45×10^{-4}, (ii) 0.30 mol $L^{-1}t^{-1}$

8. 0.022 hr^{-1}

9. 7.097×10^8 years

◆ ◆ ◆

New Questions

9. In a catalytic conversion of N_2 to NH_3 by Haber's process, the rate of reaction was expressed as change in the concentration of ammonia per time is $40\times10^{-3}\ mol litre^{-1}s^{-1}$. If there are no side reaction, the rate of the reaction as expressed in terms of hydrogen is (in *mol* $litre^{-1}s^{-1}$)

(a) 60×10^{-3} (b) 20×10^{-3}

(c) 1.200 (d) 10.3×10^{-3}

10. If the concentration of the reactants is increased, the rate of reaction **[MP PMT 1989]**

(a) Remains unaffected (b) Increases

(c) Decreases (d) May increase or decrease

11. Time required for completion of ionic reactions in comparison to molecular reactions is

(a) Maximum (b) Minimum

(c) Equal (d) None

12. For reaction $2A+B\rightarrow$ products, the active mass of *B* is kept constant and that of *A* is doubled. The rate of reaction will then **[MP PET 1993]**

(a) Increase 2 times (b) Increase 4 times

(c) Decrease 2 times (d) Decrease 4 times

13. In a reaction $2A+B\rightarrow A_2B$, the reactant *A* will disappear at

[MP PET 1993]

(a) Half the rate that *B* will decrease

(b) The same rate that *B* will decrease

(c) Twice the rate that *B* will decrease

(d) The same rate that A_2B will form

14. The rate of a gaseous reaction is given by the expression $K[A][B]$. If the volume of the reaction vessel is suddenly reduced to 1/4th of the initial volume, the reaction rate relating to original rate will be **[Roorkee 1992]**

(a) 1/10 (b) 1/8

(c) 8 (d) 16

15. A catalyst increases the rate of reaction because it

[EAMCET 1992]

(a) Increases the activation energy

(b) Decreases the energy barrier for reaction

(c) Decreases the collision diameter

(d) Increases the temperature coefficient

16. For the reaction $N_2(g)+3H_2(g)\rightarrow 2NH_3(g)$ under certain conditions of temperature and partial pressure of the reactants, the rate of formation of NH_3 is $0.001 kg h^{-1}$. The rate of conversion of H_2 under the same conditions is

[IIT 1994]

(a) $1.82\times10^{-4}\ kg/hr$ (b) $0.0015 kg/hr$

(c) $1.52\times10^{4}\ kg/hr$ (d) $1.82\times10^{-14}\ kg/hr$

17. In the reaction $2A+B\rightarrow A_2B$, if the concentration of A is doubled and of B is halved, then the rate of the reaction will

[MP PET 1994; CBSE PMT 2000]

(a) Increase by four times (b) Decrease by two times

(c) Increase by two times (d) Remain the same

18. The term $\left(-\frac{dc}{dt}\right)$ in a rate equation refers to the

[MP PMT 1996]

(a) Concentration of the reactant

(b) Decrease in concentration of the reactant with time

(c) Increase in concentration of the reactant with time

(d) Velocity constant of the reaction

19. The rate of a reaction depends upon the **[Pb. PMT 1999]**

(a) Volume

(b) Force

(c) Pressure

(d) Concentration of reactant

20. For a given reaction $3A+B\rightarrow C+D$ the rate of reaction can be represented by **[DCE 2000]**

(a) $-\frac{1}{3}\frac{d[A]}{dt}=\frac{-d[B]}{dt}=\frac{+d[C]}{dt}=\frac{+d[D]}{dt}$

(b) $-\frac{1}{3}\frac{d[A]}{dt}=\frac{d[C]}{dt}=K[A]^m[B]^n$

(c) $+\frac{1}{3}\frac{d[A]}{dt}=\frac{-d[C]}{dt}=K[A]^n[B]^m$

(d) None of these

21. For the reaction $N_2+3H_2\rightarrow 2NH_3$

if $\frac{\Delta[NH_3]}{\Delta t}=2\times10^{-4}mol l^{-1}s^{-1}$, the value of $\frac{-\Delta[H_2]}{\Delta t}$ would be

[MP PMT 2000]

(a) $1\times10^{-4}mol\ l^{-1}s^{-1}$ (b) $3\times10^{-4}mol\ l^{-1}s^{-1}$

(c) $4\times10^{-4}mol\ l^{-1}s^{-1}$ (d) $6\times10^{-4}mol l^{-1}s^{-1}$

22. A gaseous hypothetical chemical equation $2A\rightleftharpoons 4B+C$ is carried out in a closed vessel. The concentration of *B* is found to increase by $5\times10^{-3}mol\ l^{-1}$ in 10 second. The rate of appearance of *B* is **[AFMC 2001]**

(a) $5\times10^{-4}mol\ l^{-1}sec^{-1}$ (b) $5\times10^{-5}mol\ l^{-1}sec^{-1}$

(c) $6\times10^{-5} mol\, l^{-1}\sec^{-1}$ (d) $4\times10^{-4} mol l^{-1}\sec^{-1}$

23. The rate of a chemical reaction depends upon **[AFMC 2002]**

(a) Time (b) Pressure

(c) Concentration (d) All of these

24. The rate of disappearance of SO_2 in the reaction $2SO_2+O_2\rightarrow 2SO_3$ is $1.28\times10^{-3} g/sec$ then the rate of formation of SO_3 is **[JIPMER 2002]**

(a) $0.64\times10^{-3} g/sec$ (b) $0.80\times10^{-3} g/sec$

(c) $1.28\times10^{-3} g/sec$ (d) $1.60\times10^{-3} g/sec$

25. When the concentration of *A* in the reaction $A+B\rightleftharpoons AB$ is doubled, the rate of reaction will be **[MP PMT 2002]**

(a) Doubled (b) Decreased by half

(c) Unchanged (d) Increased by four times

26. The velocity of the chemical reaction doubles every 10^oC rise of temperature. If the temperature is raised by 50^oC, the velocity of the reaction increases to about

(a) 32 times (b) 16 times

(c) 20 times (d) 50 times

27. An increase in temperature by 10^oC, generally increases the rate of a reaction by

(a) 2 times (b) 10 times

(c) 9 times (d) 100 times

28. The temperature coefficient for reaction in which food deteriorates is 2. Then food deteriorates ...... times as rapidly at 25^oC as it does at 5^oC

(a) Two (b) Four

(c) Six (d) Twenty

29. The rate of a reaction is doubled for every 10^o rise in temperature. The increase in reaction rate as a result of temperature rise from 10^o to 100^o is **[KCET 1993; Kerala PET 2002; MP PET 2003]**

(a) 112 (b) 512

(c) 400 (d) 614

30. A catalyst increases the rate of a chemical reaction by **[MNR 1988; CPMT 1999; Pb. PMT 2000]**

(a) Increasing the activation energy

(b) Decreasing the activation energy

(c) Reacting with reactants

(d) Reacting with products

31. Velocity constant of a reaction at 290 *K* was found to be 3.2×10^{-3}. At 310 *K* it will be about **[KCET 1989, 91]**

(a) 1.28×10^{-2} (b) 9.6×10^{-3}

(c) 6.4×10^{-3} (d) 3.2×10^{-4}

32. The temperature coefficient of a reaction is

(a) Specific reaction rate at 25^oC

(b) Rate of the reaction at 100^oC

(c) Ratio of the rate constants at temperatures 35^oC and 25^oC

(d) Ratio of the rate constants at two temperatures differing by 1^oC

33. The main function of a catalyst in speeding up a reaction is

(a) To increase the rate of the forward reaction

(b) To change the reaction path so as to decrease the energy of activation for the reaction

(c) To reduce the temperature at which the reaction can occur

(d) To increase the energy of the molecules of the reactants

34. The rate of a reaction **[CPMT 1973]**

(a) Increases with increase in temperature

(b) Decreases with increase in temperature

(c) Does not depend on temperature

(d) Does not depend on concentration

35. Which of the following statements is false in relation to enzyme **[MP PMT 2003]**

(a) *pH* affects their functioning

(b) Temperature affects their functioning

(c) They always increase activation energy

(d) Their reactions are specific

36. A reaction is catalysed by *'X'*. Here *'X'* **[MP PMT 2003]**

(a) Decreases the rate constant of reaction

(b) Does not affect the equilibrium constant of reaction

(c) Decreases the enthalpy of reaction

(d) Decreases the activation energy

37. Which reaction characteristics are changing by the addition of a catalyst to a reaction at constant temperature

(i) Activation energy (ii) Equilibrium constant

(iii) Reaction entropy (iv) Reaction enthalpy

[DCE 2003]

(a) (i) Only (b) (iii) only

(c) (i) and I(ii) only (d) All of these

38. The velocity constant of a reaction at 290 *K* was found to be 3.2×10^{-3}. At 300 *K* it will be **[MP PMT 2004]**

(a) 1.28×10^{-2} (b) 6.4×10^{-3}

(c) 9.6×10^{-3} (d) 3.2×10^{-4}

39. In which of the following cases, does the reaction go farthest to completion **[UPSEAT 2001]**

(a) $K = 10^3$ (b) $K = 10^{-2}$

(c) $K = 10$ (d) $K = 1$

40. Rate of reaction **[Pb. CET 2004]**

(a) Decreases with increase in temperature

(b) Increases with increase in temperature

(c) May increase or decrease with increase in temperature

(d) Does not depend on temperature

41. For the reaction $2N_2O_{5(g)} \rightarrow 4NO_{2(g)} + O_{2(g)}$, if concentration of NO_2 in 100 seconds is increased by $5.2 \times 10^{-3} m$. Then rate of reaction will be

[Kerala CET 2005]

(a) $1.3 \times 10^{-5} ms^{-1}$ (b) $5 \times 10^{-4} ms^{-1}$

(c) $7.6 \times 10^{-4} ms^{-1}$ (d) $2 \times 10^{-3} ms^{-1}$

(e) $2.5 \times 10^{-5} ms^{-1}$

42. A first order reaction complete its 10% in 20 minutes then time required to complete its 19% is **[Kerala CET 2005]**

(a) 30 minutes (b) 40 minutes

(c) 50 minutes (d) 38 minutes

(e) 45 minutes

Rate law and Rate constant

1. Which of these does not influence the rate of reaction **[KCET 2005]**

(a) Nature of the reactants

(b) Concentration of the reactants

(c) Temperature of the reaction

(d) Molecularity of the reaction

2. The rate law for reaction $A + 2B = C + 2D$ will be

(a) Rate $= K[A][B]$ (b) Rate $= K[A][2B]$

(c) Rate $= K[A][B]^2$ (d) Rate $= K\dfrac{[C][D]^2}{[A][B]^2}$

3. In the reaction $2N_2O_5 \rightarrow 4NO_2 + O_2$, initial pressure is $500\,atm$ and rate constant K is $3.38 \times 10^{-5}\ \sec^{-1}$. After 10 minutes the final pressure of N_2O_5 is **[Orissa JEE 2005]**

(a) 490 atm (b) 250 atm

(c) 480 atm (d) 420 atm

4. The rate law for the reaction

Sucrose + Water $\xrightarrow{[H^+]}$ Glucose + Fructose is given by

(a) Rate $= K$ [sucrose] [water]

(b) Rate $= K$ [sucrose] $[\text{water}]^0$

(c) Rate $= K$ $[\text{sucrose}]^0$ [water]

(d) Rate $= K$ $[\text{sucrose}]^{1/2}$ $[\text{water}]^{1/2}$

5. $A + 2B \rightarrow C + D$. If $-\dfrac{d[A]}{dt} = 5 \times 10^{-4} mol\,l^{-1} s^{-1}$ 1, then $-\dfrac{d[B]}{dt}$ is **[DPMT 2005]**

(a) $2.5 \times 10^{-4} mol\,l^{-1} s^{-1}$ (b) $5.0 \times 10^{-4} mol\,l^{-1} s^{-1}$

(c) $2.5 \times 10 - 3 mol\,l^{-1} s^{-1}$ (d) $1.0 \times 10^{-3} mol\,l^{-1} s^{-1}$

6. **The data for the reaction $A + B \rightarrow C$ is** **[CBSE PMT 1994]**

Exp.	$[A]_0$	$[B]_0$	Initial rate
(1)	0.012	0.035	0.10
(2)	0.024	0.070	0.80
(3)	0.024	0.035	0.10
(4)	0.012	0.070	0.80

The rate law corresponds to the above data is

(a) Rate $= k[B]^3$ (b) Rate $= k[B]^4$

(c) Rate $= k[A][B]^3$ (d) Rate $= k[A]^2[B]^2$

7. The experimental data for the reaction $2A + B_2 \rightarrow 2AB$ is

[CBSE PMT 1997]

Exp.	$[A]_0$	$[B]_0$	Rate (mole s^{-1})
(1)	0.50	0.50	1.6×10^{-4}
(2)	0.50	1.00	3.2×10^{-4}
(3)	1.00	1.00	3.2×10^{4}

The rate equation for the above data is

(a) Rate $= k[B_2]$ (b) Rate $= k[B_2]^2$

(c) Rate $= k[A]^2[B]^2$ (d) Rate $= k[A]^2[B]$

8. The reaction $2NO(g) + O_2(g) \rightleftharpoons 2NO_2(g)$ is of first order. If volume of reaction vessel is reduced to 1/3, the rate of reaction would be **[MP PMT 2001]**

(a) 1/3 *times* (b) 2/3 *times*

(c) 3 *times* (d) 6 *times*

9. For a reaction $2A + B \rightarrow$ Products, doubling the initial concentration of both the reactants increases the rate by a factor of 8, and doubling the concentration of *B* alone doubles the rate. The rate law for the reaction is

[MP PET 2001]

(a) $\gamma = k[A][B]^2$ (b) $\gamma = k[A]^2[B]$

(c) $\gamma = k[A][B]$ (d) $\gamma = k[A]^2[B]^2$

10. For a reactions $A + B \rightarrow$ product, it was found that rate of reaction increases four times if concentration of '*A*' is doubled, but the rate of reaction remains unaffected. If concentration of '*B*' is doubled. Hence, the rate law for the reaction is **[MP PET/PMT 1998; MP PMT 2003]**

(a) rate $= k[A][B]$ (b) rate $= k[A]^2$

(c) rate $= k[A]^2[B]^1$ (d) rate $= k[A]^2[B]^2$

11. Velocity constant K of a reaction is affected by

(a) Change in the concentration of the reactant

(b) Change of temperature

(c) Change in the concentration of the product

(d) None of the above

12. Point out the wrong statement :

For a first order reaction

(a) Time for half-change $(t_{1/2})$ is independent of initial concentration

(b) Change in the concentration unit does not change the rate constant (K)

(c) Time for half-change $\times$ rate constant $= 0.693$

(d) The unit of K is $mole^{-1}\ \text{min}^{-1}$

13. The rate constant of a reaction depends on **[CPMT 1989; DPMT 2001]**

(a) Temperature (b) Mass

(c) Weight (d) Time

14. In a first order reaction the concentration of reactant decreases from $800 mol/dm^3$ to $50 mol/dm^3$ is 2×10^2 sec. The rate constant of reaction in sec^{-1} is **[IIT-JEE (Screening) 2003]**

(a) 2×10^4 (b) 3.45×10^{-5}

(c) 1.386×10^{-2} (d) 2×10^{-4}

15. For a reaction $A \rightarrow B$, the rate of reaction quadrupled when the concentration of A is doubled. The rate expression of the reaction is $r = K(A)^n$. when the value of n is

(a) 1 (b) 0

(c) 3 (d) 2

16. The velocity constant of a reaction is *K*. Which of the following statements is not true regarding *K*

(a) *K* is a constant for a reaction at a given temperature

(b) The value of *K* changes when the temperature changes

(c) *K* is the velocity of the reaction at unit concentrations of the reactant

(d) *K* is a constant for all reactions

17. For the following reaction scheme (homogeneous), the rate constant has units : $A + B \xrightarrow{K} C$ **[MP PET 1999]**

(a) $\text{sec}^{-1}\ mole$ (b) sec^{-1}

(c) $\text{sec}^{-1}\ litre\ mole^{-1}$ (d) *sec*

18. Which of the following oxides of nitrogen will be the most stable one **[NCERT 1978]**

(a) $2NO_2(g) \rightleftharpoons N_2(g) + 2O_2(g); K = 6.7 \times 10^{16} mol l^{-1}$

(b) $2NO(g) \rightleftharpoons N_2(g) + O_2(g); K = 2.2 \times 10^{30} mol l^{-1}$

(c) $2N_2O_5(g) \rightleftharpoons 2N_2(g) + 5O_2(g); K = 1.2 \times 10^{34}\ mol l^{-5}$

(d) $2N_2O(g) \rightleftharpoons 2N_2(g) + O_2(g); K = 3.5 \times 10^{33}\ mol litre^{-1}$

19. The rate of reaction is determined by slow step reaction. The step is called

(a) Reaction rate (b) Activation step

(c) Rate determining step (d) None of the above

20. The rate of the reaction $CCl_3CHO + NO \rightarrow CHCl_3 + NO + CO$ is given by Rate $= K[CCl_3CHO][NO]$. If concentration is expressed in moles/litre, the units of *K* are **[MP PET 1993]**

(a) $litre^2\ mole^{-2}\ \text{sec}^{-1}$ (b) $mole litre^{-1}\ \text{sec}^{-1}$

(c) $litre mole^{-1}\ \text{sec}^{-1}$ (d) sec^{-1}

21. Rate constant for a reaction $H_2 + I_2 \rightarrow 2HI$ is 49, then rate constant for reaction $2HI \rightarrow H_2 + I_2$ is **[Bihar MEE 1997]**

(a) 7 (b) 1/49

(c) 49 (d) 21

(e) 63

22. The reaction

$$N_2O_5\,(\text{in } CCl_4 \text{ solution}) \rightarrow 2NO_2(\text{solution}) + \frac{1}{2}O_2(g)$$

is of first order in N_2O_5 with rate constant $6.2 \times 10^{-1} s^{-1}$. What is the value of rate of reaction when $[N_2O_5] = 1.25 mole l^{-1}$ **[AFMC 1998]**

(a) $7.75\times10^{-1} mole l^{-1}s^{-1}$ (b) $6.35\times10^{-3} mole l^{-1}s^{-1}$

(c) $5.15\times10^{-5} mole l^{-1}s^{-1}$ (d) $3.85\times10^{-1} mole l^{-1}s^{-1}$

23. A reaction that is of the first order with respect to reactant *A* has a rate constant $6\,\text{min}^{-1}$. If we start with $[A]=0.5 mol\ l^{-1}$, when would $[A]$ reach the value 0.05*mol* l^{-1} **[KCET 2000]**

(a) 0.384 *min* (b) 0.15 *min*

(c) 3 *min* (d) 3.84 *min*

24. The rate constant for the reaction, $2N_2O_5 \rightarrow 4NO_2 + O_2$ is $3\times10^{-5}\,\text{sec}^{-1}$. If the rate is $2.40\times10^{-5} mol\ litre^{-1}\ \text{sec}^{-1}$. Then the concentration of N_2O_5 (in *mol litre*$^{-1}$) is **[IIT Screening 2000]**

(a) 1.4 (b) 1.2

(c) 0.04 (d) 0.8

25. For the reaction $2N_2O_5 \rightarrow 4NO_2 + O_2$ rate of reaction and rate constant are 1.02×10^{-4} and $3.4\times10^{-5}\,\text{sec}^{-1}$ respectively. The concentration of N_2O_5 at that time will be **[BHU 2001]**

(a) 1.732 (b) 3

(c) 1.02×10^{-4} (d) 3.4×10^{5}

26. The rate law of the reaction $2N_2O_5 \rightarrow 4NO_2 + O_2$ is **[MP PET 2002]**

(a) $r=K[N_2O_5]$ (b) $r=K[N_2O_5]^2$

(c) $r=K[N_2O_5]^0$ (d) $r=K[NO_2]^4[O_2]$

27. If $R=K[NO]^2[O_2]$, rate constant may be increased by **[BHU 2003]**

(a) Increasing temperature

(b) Decreasing temperature

(c) Increasing concentration of O_2

(d) Increasing concentration of NO

28. The value of rate constant $A+B\rightarrow$ products depends on **[BHU 2003]**

(a) Concentration of *A* and *B*

(b) Pressure

(c) Temperature

(d) All of these

29. The rate constant of a reaction depends upon **[BHU 2004]**

(a) Extent of reaction

(b) Time of reaction

(c) Temperature of the system

(d) Concentration of the system

30. The rate equation for the reaction $2A+B\rightarrow C$ is found to be: rate $=k[A][B]$. The correct statement in relation to this reaction is that the **[AIEEE 2004]**

(a) Rate of formation of *C* is twice the rate of disappearance of A

(b) $t_{1/2}$ is a constant

(c) Unit of *k* must be s^{-1}

(d) Value of *k* is independent of the initial concentrations of *A* and *B*

31. The specific rate constant of a first order reaction depends on the **[IIT 1981, 83; DPMT 1991; Bihar MEE 1995; KCET 1998]**

(a) Concentration of the reactants

(b) Concentration of the products

(c) Time of reaction

(d) Temperature of reaction

32. If the concentration is expressed in moles per litre, the unit of the rate constant for a first order reaction is **[MNR 1986; MP PET 1994, 2000, 01;Bihar MEE 1996; CPMT 1997; MP PMT 1995, 96, 99;AFMC 2002]**

(a) *mole litre* $^{-1}\,\text{sec}^{-1}$ (b) *mole litre* $^{-1}$

(c) sec^{-1} (d) mole $^{-1}$ *litre* $^{-1}$ *sec* $^{-1}$

33. The dimension of rate constant of a second order reaction involves **[NCERT 1982]**

(a) Neither time nor concentration

(b) Only time

(c) Time and concentration

(d) Time and square of concentration

34. The unit of rate constant of second order reaction is usually expressed as **[NCERT 1983, 84; MNR 1983; MP PMT 1994, 99]**

(a) *mole litre* sec^{-1} (b) $mole^{-1}\ litre^{-1}\ \text{sec}^{-1}$

(c) $mole litre^{-1}\ \text{sec}^{-1}$ (d) $mole^{-1}\ litre \text{sec}^{-1}$

35. A zero order reaction is one whose rate is independent of **[NCERT 1981]**

(a) Temperature of the reaction

(b) The concentrations of the reactants

(c) The concentration of the products

(d) The material of the vessel in which the reaction is carried out

36. The unit of rate constant for a zero order reaction is **[NCERT 1981; MP PMT 2000; RPET 2000]**

(a) *litre* sec^{-1} (b) *litre* $mole^{-1}\ \text{sec}^{-1}$

(c) *mole* $litre^{-1}\ \text{sec}^{-1}$ (d) *mole* sec^{-1}

37. Which of the following rate laws has an overall order of 0.5 for reaction involving substances X, Y and Z **[AIIMS 1983]**

(a) Rate $= K(C_x)(C_y)(C_z)$

(b) Rate $= K(C_x)^{0.5}(C_y)^{0.5}(C_z)^{0.5}$

(c) Rate $= K(C_x)^{1.5}(C_y)^{-1}(C_z)^{0}$

(d) Rate $= K(C_x)(C_z)^{n}/(C_y)^{2}$

38. The rates of a certain reaction (*dc/dt*) at different times are as follows

Time	Rate (*mole litre*$^{-1}$ *sec* $^{-1}$)
0	2.8×10^{-2}
10	2.78×10^{-2}
20	2.81×10^{-2}
30	2.79×10^{-2}

The reaction is **[NCERT 1978]**

(a) Zero order (b) First order

(c) Second order (d) Third order

39. For a chemical reaction $A \rightarrow B$ it is found that the rate of reaction doubles, when the concentration of A is increased four times. The order in A for this reaction is **[NCERT 1979; AIIMS 1997; J & K CET 2005]**

(a) Two (b) One

(c) Half (d) Zero

40. The following data are for the decomposition of ammonium nitrate in aqueous solution

Volume of N_2 in cc	Time (minutes)
6.25	10
9.50	15
11.42	20
13.65	25
35.05	Finally

The order of the reaction is **[NCERT 1980]**

(a) Zero (b) One

(c) Two (d) Three

41. The hydrolysis of ethyl acetate is a reaction of **[MP PMT 1987]**

$$CH_3COOEt + H_2O \xrightarrow{H^+} CH_3COOH + EtOH$$

(a) First order (b) Second order

(c) Third order (d) Zero order

42. The rate of reaction between A and B increases by a factor of 100, when the concentration of A is increased 10 folds. The order of reaction with respect to A is **[CPMT 1985]**

(a) 10 (b) 1

(c) 4 (d) 2

43. Which of the following is a first order reaction **[MP PMT 1987]**

(a) $NH_4NO_2 \rightarrow N_2 + 2H_2O$

(b) $2HI \rightarrow H_2 + I_2$

(c) $2NO_2 \rightarrow 2NO + O_2$

(d) $2NO + O_2 \rightarrow 2NO_2$

44. The inversion of cane sugar is represented by

$$C_{12}H_{22}O_{11} + H_2O \rightarrow C_6H_{12}O_6 + C_6H_{12}O_6$$

It is a reaction of **[AFMC 1982; MP PMT 1993; RPET 2000]**

(a) Second order (b) Unimolecular

(c) Pseudo unimolecular (d) None of the three

45. Which one of the following formula represents a first order reaction **[MP PMT 1999]**

(a) $K = \frac{x}{t}$ (b) $K = \frac{1}{2t}\left[\frac{1}{(a-x)^2} - \frac{1}{a^2}\right]$

(c) $K = \frac{2.303}{t}\log_{10}\frac{a}{(a-x)}$ (d) $K = \frac{1}{t}\frac{x}{a(a-x)}$

46. The first order rate constant for the decomposition of N_2O_5 is $6.2 \times 10^{-4}\ \text{sec}^{-1}$. The half life period for this decomposition in seconds is **[MNR 1991; MP PET 1997; UPSEAT 2000]**

(a) 1117.7 (b) 111.7

(c) 223.4 (d) 160.9

47. A first order reaction which is 30% complete in 30 minutes has a half-life period of **[AIIMS 1998]**

(a) 24.2 *min* (b) 58.2 *min*

(c) 102.2 *min* (d) 120.2 *min*

48. The order of a reaction which has the rate expression $\frac{dc}{dt} = K[E]^{3/2}[D]^{3/2}$ is

(a) 3/2 (b) 3

(c) 2 (d) 0

49. The reaction $2N_2O_5 \rightleftharpoons 2NO_2 + O_2$ follows first order kinetics. Hence, the molecularity of the reaction is

(a) Unimolecular

(b) Pseudo–unimolecular

(c) Bimolecular

(d) None of the above

50. A reaction involving two different reactants **[KCET 1989; AIEEE 2005]**

(a) Can never be a second order reaction

(b) Can never be a unimolecular reaction

(c) Can never be a bimolecular reaction

(d) Can never be a first order reaction

51. By “the overall order of a reaction”, we mean

(a) The number of concentration terms in the equation for the reaction

(b) The sum of powers to which the concentration terms are raised in the velocity equation

(c) The least number of molecules of the reactants needed for the reaction

(d) The number of reactants which take part in the reaction

52. Catalyst decomposition of hydrogen peroxide is a …….. order reaction

(a) First (b) Second

(c) Third (d) Zero

53. The half life of a first order reaction is

(a) Independent of the initial concentration of the reactant

(b) Directly proportional to the initial concentration of the reactants

(c) Inversely proportional to the initial concentration of the reactant

(d) Directly proportional to the square of the initial concentration of the reactant

54. The decomposition of N_2O_5 is a first order reaction represented by $N_2O_5 \to N_2O_4 + \frac{1}{2}O_2$. After 15 *minutes* the volume of O_2 produced is $9 ml$ and at the end of the reaction $35 ml$. The rate constant is equal to

[MP PET 1995]

(a) $\frac{1}{15}\ln\frac{35}{44}$ (b) $\frac{1}{15}\ln\frac{44}{26}$

(c) $\frac{1}{15}\ln\frac{44}{35}$ (d) $\frac{1}{15}\ln\frac{35}{26}$

55. The unit of specific reaction rate constant for a first order (if the concentration expressed in molarity) would be

[MNR 1988; UPSEAT 2000, 01]

(a) *mole* $litre^{-1}s^{-1}$ (b) *mole* $litre^{-1}$

(c) *mole* s^{-1} (d) s^{-1}

56. A first order reaction requires 30 minutes for 50% completion. The time required to complete the reaction by 75% will be

(a) 45 minutes (b) 15 minutes

(c) 60 minutes (d) None of these

57. Inversion of canesugar in dilute acid (conversion into glucose and fructose) is a

(a) Unimolecular reaction

(b) Bimolecular reaction

(c) Trimolecular reaction

(d) Pseudo-unimolecular reaction

58. The half life period of a first order reaction **[AMU 2000]**

(a) $\frac{0.693}{t}$ (b) $\frac{0.693}{K}$

(c) $\frac{2.303}{t}$ (d) $\frac{0.303}{K_1}$

59. The order of a reaction is said to be 2 with respect to a reactant *X*, when **[DPMT 2000]**

(a) The rate of the reaction is proportional to [*X*]

(b) The rate of the reaction is proportional $[X]^2$

(c) Two molecules of *X* are present in the stoichiometric equation

(d) The reaction occurs in two steps

60. Decay constant of a reaction is $1.1\times10^{-9}/sec$, then the half life of the reaction is

(a) 1.2×10^{8} (b) 6.3×10^{8}

(c) 3.3×10^{8} (d) 2.1×10^{8}

61. If the half life period of a reaction is inversely proportional to the initial concentration, the order of the reaction is

(a) Zero (b) One

(c) Two (d) Three

62. Which one of the following statements is wrong

(a) Molecularity of a reaction is always a whole number

(b) Order and molecularity of a reaction need not be same

(c) Order of a reaction may be zero

(d) Order of a reaction depends upon the mechanism of the reaction

63. The velocity constant of first order reaction is expressed in the units

(a) Concentration per unit time

(b) Time per unit concentration

(c) Per unit time

(d) Unit time per unit concentration

64. For reation, $A + B \to$ products, it is found that the rate of the reaction is proportional to the concentration of *A*, but it is independent of the concentration of B, then

(a) The order of the reaction 2 and molecularity 1

(b) Molecularity of the reaction is 2 but order is 1

(c) Order is 2 and molecularity is 2

(d) Order of the reaction is 2 but molecularity is 0

65. For a zero order reaction

(a) The concentration of the reactant does not change during the reaction

(b) The concentration change only when the temperature changes

(c) The rate remains constant throughout

(d) The rate of the reaction is proportional to the concentration

66. If '*a*' is the initial concentration and '*n*' is the order of the reaction and the half life period is '*T*', then **[MH CET 2000]**

(a) $T \propto a^{n-1}$ (b) $T \propto a^{n}$

(c) $T \propto \frac{1}{a^{n}}$ (d) $T \propto \frac{1}{a^{n-1}}$

67. In presence of HCl, sucrose gets hydrolysed into glucose and fructose. The concentration of sucrose was found to reduce form 0.4 *M* to 0.2 *M* in 1 hour and 0.1 *M* in 2 hours. The order of the reaction is

(a) Zero (b) One

(c) Two (d) None of these

68. The time of half change of a first order reaction in .... initial concentration

(a) Proportional to

(b) Inversely proportional to

(c) Independent of

(d) Equal to

69. Half life period of a first order reaction is 138.6 minutes. The velocity constant of the reaction is

(a) $0.05\,min^{-1}$ (b) $0.00005\,min^{-1}$

(c) $0.005\,min^{-1}$ (d) $200\,min^{-1}$

70. An example of a pseudo –unimolecular reaction is

(a) Dissociation of hydrogen iodide

(b) Hydrolysis of methyl acetate in dilute solution

(c) Dissociation of phosphorus pentachloride

(d) Decomposition of hydrogen peroxide

71. About half life period of a first order reaction, which one of the following statements is generally false

(a) It is independent of initial concentration

(b) It is independent of temperature

(c) It decreases with the introduction of a catalyst

(d) It increases with increase of temperature

72. Decomposition of nitrogen pentoxide is known to be a first order reaction 75 percent of the oxide had decomposed in the first 24 minutes. At the end of an hour, after the start of the reaction, the amount of oxide left will be

(a) Nil (b) About 1%

(c) About 2% (d) About 3%

73. A reaction $2A \to$ products is found to follow zero oder kinetics, then

(a) $\frac{dx}{dt} = k[A]^2$ (b) $\frac{dx}{dt} = k[A]^0$

(c) $\frac{dx}{dt} = k[A]$ (d) $\frac{dx}{dt} = k[2A]$

74. The alkaline hydrolysis of ethyl acetate is represented by the equation

$$CH_3COOC_2H_5 + NaOH \to CH_3COONa + C_2H_5OH$$

Experimentally it is found that for this reaction

$$\frac{dx}{dt} = k[CH_3COOC_2H_5][NaOH]$$

Then the reaction is **[JIPMER 1999]**

(a) Bimolecular and of first order

(b) Bimolecular and of second order

(c) Pseudo–bimolecular

(d) Pseudo–unimolecular

75. For the reaction $2HI \rightleftharpoons H_2 + I_2$, the rate of the reaction is proportional to $[HI]^2$. This means that the reaction is

[AMU 1985; MP PET 2000]

(a) Unimolecular (b) Bimolecular

(c) Of first order (d) Of second order

76. Inversion of sucrose is **[AMU 1988; MP PET 2000]**

(a) Zero order reaction (b) First order reaction

(c) Second order reaction (d) Third order reaction

77. The one which is unimolecular reaction is

[MP PMT 1999; UPSEAT 2001]

(a) $2HI \to H_2 + I_2$ (b) $N_2O_5 \to N_2O_4 + \frac{1}{2}O_2$

(c) $H_2 + Cl_2 \to 2HCl$ (d) $PCl_3 + Cl_2 \to PCl_5$

78. Integrated velocity equation for first order reaction is

(a) $[A]_o = [A]e^{-Kt}$ (b) $K = [A]_o e^{-A/t}$

(c) $Kt = 2.303\log\frac{[A]_o}{[A]}$ (d) $\log\frac{[A]_o}{[A]} = -2.303Kt$

79. If the surface area of the reactants increases, then order of the reaction

(a) Increases

(b) Decreases

(c) Remain constant

(d) Sometimes increases and sometimes dereases

80. Half life period $t_{1/2}$ for first order reaction is

(a) K (b) $\frac{1.303 \log 2}{K}$

(c) $\frac{2.303 \log 2}{K}$ (d) $\frac{9}{K}$

81. Molecularity of reaction of inversion of sugar is

(a) 3 (b) 2

(c) 1 (d) 0

82. For any reaction, if we plot a graph between time *'t'* and $\log(a-x)$, a simple line is obtained. The order of reaction is

(a) Zero (b) One

(c) Two (d) Three

83. Value of velocity constant for first order reaction is $3.46 \times 10^{-3} \text{ min}^{-1}$, the time for half change is

(a) 100 minutes (b) 400 minutes

(c) 200 minutes (d) 346 minutes

84. The unit of the velocity constant in case of zero order reaction is **[CPMT 1994]**

(a) $Conc. \times time^{-1}$ (b) $Conc.^{-1} \times time$

(c) $Conc.^{-1} \times time^{-1}$ (d) $Conc. \times (time)^2$

85. For the reaction $H_2(g) + Br_2(g) \rightarrow 2HBr(g)$, the experimental data suggest, rate $= K[H_2][Br_2]^{1/2}$. The molecularity and order of the reaction are respectively

[CPMT 1988; MP PET 1993]

(a) $2, \frac{3}{2}$ (b) $\frac{3}{2}, \frac{3}{2}$

(c) 1, 1 (d) $1, \frac{1}{2}$

86. The incorrect order indicated against the rate of reaction $A + B \xrightarrow{K} C$ is **[BHU 1990]**

	Rate	Order
(a)	$\frac{d[C]}{dt} = K[A]$	1
(b)	$\frac{d[C]}{dt} = K[A][B]$	2
(c)	$\frac{-d[A]}{dt} = K[A][B]^0$	2
(d)	$\frac{-d[A]}{dt} K[A]$	1

87. Which of the following statements regarding the molecularity of a reaction is wrong **[CBSE PMT 1989]**

(a) It is the number of molecules of the reactants taking part in a single step chemical reaction

(b) It is calculated from the reaction mechanism

(c) It may be either a whole number or fractional

(d) It depends on the rate determining step in the reaction

88. Diazonium salt decomposes as

$C_6H_5N_2^+Cl^- \rightarrow C_6H_5Cl + N_2$

At $0^\circ C$, the evolution of N_2 becomes two times faster when the initial concentration of the salt is doubled. Therefore, it is **[MNR 1994; UPSEAT 2002]**

(a) A first order reaction

(b) A second order reaction

(c) Independent of the initial concentration of the salt

(d) A zero order reaction

89. In the reaction $A + B \rightarrow$ Products, if B is taken in excess, then it is an example of **[EAMCET 1992]**

(a) Second order reaction

(b) Zero order reaction

(c) Pseudounimolecular reaction

(d) First order reaction

90. The half life of a first order reaction is $69.35 \sec$. The value of the rate constant of the reaction is **[CBSE PMT 1990]**

(a) $1.0 s^{-1}$ (b) $0.1 s^{-1}$

(c) $0.01 s^{-1}$ (d) $0.001 s^{-1}$

91. The half life for the reaction $N_2O_5 \rightleftharpoons 2NO_2 + \frac{1}{2}O_2$ in $24 hrs$ at $30^\circ C$. Starting with $10 g$ of N_2O_5 how many grams of N_2O_5 will remain after a period of 96 *hours*

[KCET 1992]

(a) $1.25 g$ (b) $0.63 g$

(c) $1.77 g$ (d) $0.5 g$

92. The half life of a first order reaction is 10 minutes. If initial amount is $0.08 mol/litre$ and concentration at some instant is $0.01 mol/litre$, then $t =$ **[Roorkee 1990]**

(a) 10 minutes (b) 30 minutes

(c) 20 minutes (d) 40 minutes

93. Half life period of second order reaction is **[MP PMT 1994]**

(a) Proportional to the initial concentration of reactants

(b) Independent of the initial concentration of reactants

(c) Inversely proportional to initial concentration of reactants

(d) Inversely proportional to square of initial concentration of reactants

94. The reaction $2H_2O_2 \rightarrow 2H_2O + O_2$ is a **[Manipal MEE 1995]**

(a) Zero order reaction (b) First order reaction

(c) Second order reaction (d) Third order reaction

95. In a reaction involving hydrolysis of an organic chloride in presence of large excess of water

$RCl + H_2O \rightarrow ROH + HCl$ **[MP PET 1995]**

(a) Molecularity is 2, order of reaction is also 2

(b) Molecularity is 2, order of reaction is 1

(c) Molecularity is 1, order of reaction is 2

(d) Molecularity is 1, order of reaction is also 1

96. The thermal decomposition of a compound is of first order. If a sample of the compound decomposes 50% in 120 minutes, in what time will it undergo 90% decomposition

[MP PET 1996]

(a) Nearly 240 *minutes* (b) Nearly 480 *minutes*

(c) Nearly 450 *minutes* (d) Nearly 400 *minutes*

97. The order of a reaction with rate equals $kC_A^{3/2} C_B^{-1/2}$ is

[MP PET 1996, 2001]

(a) 2 (b) 1

(c) $-\frac{1}{2}$ (d) $\frac{3}{2}$

98. If the rate expression for a chemical reaction is given by Rate $= k[A]^m[B]^n$ **[MP PMT 1996]**

(a) The order of the reaction is m

(b) The order of the reaction is n

(c) The order of the reaction is $m+n$

(d) The order of the reaction is $m-n$

99. The half-life period of a first order reaction is 100 *sec*. The rate constant of the reaction is

[MP PMT 1997; MP PET 2001]

(a) $6.93 \times 10^{-3}\ \sec^{-1}$ (b) $6.93 \times 10^{-4}\ \sec^{-1}$

(c) $0.693 \sec^{-1}$ (d) $69.3 \sec^{-1}$

100. For the first order reaction with rate constant k, which expression gives the half-life period ? (Initial concentration $= a$) **[MP PET/PMT 1998]**

(a) $\frac{1^2}{k}$ (b) $\frac{1}{ka}$

(c) $\frac{0.693}{k}$ (d) $\frac{3}{2ka^2}$

101. The rate constant of a first order reaction whose half-life is 480 seconds, is **[MP PET 1999]**

(a) $2.88 \times 10^{-3}\ \sec^{-1}$ (b) $1.44 \times 10^{-3}\ \sec^{-1}$

(c) $1.44 \sec^{-1}$ (d) $0.72 \times 10^{-3}\ \sec^{-1}$

102. The conversion of $A \rightarrow B$ follows second order kinetics. Doubling the concentration of A will increase the rate of formation of B by a factor

[MP PET 1999; DCE 1999; KCET 2001; BCECE 2005]

(a) $1/4$ (b) 2

(c) $1/2$ (d) 4

103. The reaction $2FeCl_3 + SnCl_2 \rightarrow 2FeCl_2 + SnCl_4$ is an example of **[CBSE PMT 1996; MP PET 1999]**

(a) First order reaction

(b) Second order reaction

(c) Third order reaction

(d) None of these

104. If reaction between A and B to give C shows first order kinetics in A and second order in B, the rate equation can be written as **[MP PET 1999]**

(a) Rate $= k[A][B]^{1/2}$ (b) Rate $= k[A]^{1/2}[B]$

(c) Rate $= k[A][B]^2$ (d) Rate $= k[A]^2[B]$

105. For a first order reaction, the half-life period is independent of

[CBSE PMT 1999]

(a) Initial concentration

(b) Cube root of initial concentration

(c) First power of final concentration

(d) Square root of final concentration

106. Order of a reaction can have **[DPMT 1996]**

(a) $+ve$ values (b) Whole number values

(c) Fractional values (d) All of the above

107. The order of the reaction occurring by following mechanism should be **[JIPMER 1997]**

(i) $A_2 \rightarrow A + A$ (fast)

(ii) $A + B_2 \rightarrow AB + B$ (slow)

(iii) $A + B \rightarrow$ (fast)

(a) $1\frac{1}{2}$ (b) $3\frac{1}{2}$

(c) 2 (d) None of these

108. For the reaction $A \to B$, the rate law expression is : Rate $= k[A]$

Which of the following statements is incorrect

[Pb. PMT 1998]

(a) The reaction is said to follow first order kinetics

(b) The half life of the reaction will depend on the initial concentration of the reactant

(c) k is constant for the reaction at a constant temperature

(d) The rate law provides a simple way of predicting the concentration of reactants and products at any time after the start of the reaction

109. If initial concentration is reduced to its 1/4th in a zero order reaction, the time taken for half of the reaction to complete

[BHU 1998]

(a) Remains same (b) Becomes 4 times

(c) Becomes one-fourth (d) Doubles

110. For a reaction whose rate expression is :

Rate $= k[A]^{1/2}[B]^{3/2}$, the order would be **[Pune CET 1998]**

(a) 1.5 (b) 2

(c) 3 (d) 1

111. For the reaction $A \to B$, the rate increases by a factor of 2.25 when the concentration of A is increased by 1.5. What is the order of the reaction **[KCET 1998]**

(a) 3 (b) 0

(c) 2 (d) 1

112. For the reaction $H_2 + Cl_2 \xrightarrow{\text{Sunlight}} 2HCl$ taking place on water, the order of reaction is

[KCET 1998; AIIMS 2002; Pb. PMT 2002]

(a) 1 (b) 2

(c) 3 (d) 0

113. For a first order reaction, rate constant is $0.6932 hr^{-1}$, then half-life for the reaction is **[Bihar MEE 1997]**

(a) $0.01 hr$ (b) $1 hr$

(c) $2 hr$ (d) $10 hr$

(e) $0.1 hr$

114. The rate constant of a reaction is $0.69 \times 10^{-1}\ \text{min}^{-1}$ and the initial concentration is $0.2 mol l^{-1}$. The half-life period is

[AIIMS 1998]

(a) 400 *sec* (b) 600 *sec*

(c) 800 *sec* (d) 1200 *sec*

115. The rate constant of a first order reaction is 3×10^{-6} per second. If the initial concentration is 0.10 *m*, the initial rate of reaction is

[AFMC 1999 Pb. PMT 1999, 2000; BHU 1999; AIIMS 1999; KCET 2000; DCE 2004]

(a) $3 \times 10^{-5} ms^{-1}$ (b) $3 \times 10^{-6} ms^{-1}$

(c) $3 \times 10^{-8} ms^{-1}$ (d) $3 \times 10^{-7} ms^{-1}$

116. Certain bimolecular reactions which follow the first order kinetics are called **[KCET (Med.) 1999]**

(a) First order reactions

(b) Unimolecular reactions

(c) Bimolecular reactions

(d) Pseudounimolecular reactions

117. The rate law of the reaction $A + 2B \to$ Product is given by $\frac{d[dB]}{dt} = k[B^2]$. If A is taken in excess, the order of the reaction will be **[AMU (Engg.) 1999]**

(a) 1 (b) 2

(c) 3 (d) 0

118. For a first order reaction $A \to$ product, the rate of reaction at $[A] = 0.2\ mol\ l^{-1}$ is $1.0 \times 10^{-2} mol\ l^{-1}\ \text{min}^{-1}$. The half life period for the reaction is **[Roorkee 1999]**

(a) 832 *s* (b) 440 *s*

(c) 416 *s* (d) 13.86 *s*

119. For the reaction $A + B \to$ products, doubling the concentration of *A* the rate of the reaction is doubled, but on doubling the concentration of *B* rate remains unaltered. The over all order of the reaction is **[JIPMER 1999]**

(a) 1 (b) 0

(c) 2 (d) 3

120. Which among the following is a false statement

[KCET 1999]

(a) Half life of a third order reaction is inversely proportional to the square of initial concentration of the reactant.

(b) Molecularity of a reaction may be zero or fractional

(c) For a first order reaction $t_{1/2} = \frac{0.693}{K}$

(d) Rate of zero order reaction is independent of initial concentration of reactant

121. After how many seconds will the concentration of the reactants in a first order reaction be halved, if the decay constant is $1.155 \times 10^{-3}\ \text{sec}^{-1}$ **[CBSE PMT 2000]**

(a) 100 *sec* (b) 200 *sec*

(c) 400 *sec* (d) 600 *sec*

122. What is the order of a reaction which has a rate expression rate $= K[A]^{3/2}[B]^{-1}$ **[DCE 2000]**

(a) 3/2 (b) 1/2

(c) 0 (d) None of these

123. Which of the following expression is correct for first order reaction? (CO) refers to initial concentration of reactant

[DCE 2000]

(a) $t_{1/2} \propto CO$ (b) $t_{1/2} \propto CO^{-1}$

(c) $t_{1/2} \propto CO^{-2}$ (d) $t_{1/2} \propto CO^{0}$

124. For a reaction $2NO(g) + Cl_2(g) \rightleftharpoons 2NOCl(g)$. When concentration of Cl_2 is doubled, the rate of reaction becomes two times of the original. When the concentration of *NO* is doubled the rate becomes four times. What is the order of the reaction

[MP PMT 2000]

(a) 1 (b) 2

(c) 3 (d) 4

125. The rate constant for a second order reaction is $8 \times 10^{-5} M^{-1} min^{-1}$. How long will it take a 1*M* solution to be reduced to 0.5 *M* **[MH CET 2001]**

(a) 8×10^{-5} *min* (b) 8.665×10^{3} *min*

(c) 4×10^{-5} *min* (d) 1.25×10^{4} *min*

126. The rate for a first order reaction is $0.6932 \times 10^{-2} mol l^{-1} min^{-1}$ and the initial concentration of the reactants is 1*M*, $T_{1/2}$ is equal to **[JIPMER (Med.) 2001]**

(a) 6.932 *min* (b) 100 *min*

(c) 0.6932×10^{-3} *min* (d) 0.6932×10^{-2} *min*

127. For a given reaction $t_{1/2} = \frac{1}{Ka}$.. The order of the reaction is

[KCET 2001]

(a) 1 (b) 0

(c) 3 (d) 2

128. 75% of a first order reaction is completed in 30 minutes. What is the time required for 93.75% of the reaction (in minutes) **[KCET 2001]**

(a) 45 (b) 120

(c) 90 (d) 60

129. A First order reaction is half completed in 45 minutes. How long does it need 99.9% of the reaction to be completed

[AIIMS 2001]

(a) 5 hours (b) 7.5 hours

(c) 10 hours (d) 20 hours

130. A substance '*A*' decomposes by a first order reaction starting initially with [A] =2.00m and after 200 min [A] = 0.15m. For this reaction what is the value of *k* **[AIIMS 2001]**

(a) 1.29×10^{-2} min^{-1} (b) 2.29×10^{-2} min^{-1}

(c) 3.29×10^{-2} min^{-1} (d) 4.40×10^{-2} min^{-1}

131. Which of the following statements about zero order reaction is not true **[DCE 2001]**

(a) Its unit is sec^{-1}

(b) The graph between log (reactant) versus rate of reaction is a straight line

(c) The rate of reaction increases with the decrease in concentration of reactants

(d) Rate of reaction is independent of concentration of reactants

132. The given reaction $2NO + O_2 \rightarrow 2NO_2$ is an example of

[CBSE PMT 2001; JIPMER 2002]

(a) First order reaction (b) Second order reaction

(c) Third order reaction (d) None of these

133. Order of a reaction is decided by **[KCET 2002]**

(a) Pressure

(b) Temperature

(c) Molecularity

(d) Relative concentration of reactants

134. From the following which is a second order reaction

[AMU 2002]

(a) $K = 5.47 \times 10^{-4}$ sec^{-1}

(b) $K = 3.9 \times 10^{-3}$ mole lit sec^{-1}

(c) $K = 3.94 \times 10^{-4}$ lit mole^{1} sec^{-1}

(d) $K = 3.98 \times 10^{-5}$ lit mole^{2} sec^{-1}

135. For the reaction $A + 2B \rightarrow C$, rate is given by $R = [A][B]^2$ then the order of the reaction is **[AIEEE 2002]**

(a) 3 (b) 6

(c) 5 (d) 7

136. Units of rate constant of first and zero order reactions in terms of molarity *M* unit are respectively **[AIEEE 2002]**

(a) sec^{-1}, $M\ sec^{-1}$ (b) sec^{-1}, M

(c) $M\ sec^{-1}$, sec^{-1} (d) M, sec^{-1}

137. The reaction $2N_2O_5 \rightleftharpoons 2N_2O_4 + O_2$ is **[MP PMT 2002]**

(a) Bimolecular and second order

(b) Unimolecular and first order

(c) Bimolecular and first order

(d) Bimolecular and zero order

138. The half-life period for a first order reaction is 693 seconds. The rate constants for this reaction would be **[MP PET 2002]**

(a) $0.1 sec^{-1}$ (b) $0.01 sec^{-1}$

(c) $0.001 sec^{-1}$ (d) $0.0001 sec^{-1}$

139. For an elementary reaction, $2A + B \rightarrow C + D$ the molecularity is **[Kurukshetra CEE 2002]**

(a) Zero (b) One

(c) Two (d) Three

140. If the order of the reaction $x + y \xrightarrow{h\nu} xy$ is zero, it means that the rate of **[Kurukshetra CEE 2002]**

(a) Reaction is independent of temperature

(b) Formation of activated complex is zero

(c) Reaction is independent of the concentration of reacting species

(d) Decomposition of activated complex is zero

141. For a first order reaction velocity constant, $K = 10^{-3} s^{-1}$. Two third life for it would be **[MP PET 2001; UPSEAT 2003]**

(a) 1100 *s* (b) 2200 *s*

(c) 3300 *s* (d) 4400 *s*

142. In a reaction, the concentration of reactant is increased two times and three times then the increases in rate of reaction were four times and nine times respectively, order of reaction is **[UPSEAT 2003]**

(a) Zero (b) 1

(c) 2 (d) 3

143. For a chemical reaction....can never be a fraction **[EAMCET 2003]**

(a) Order (b) Half-life

(c) Molecularity (d) Rate constant

144. 75% of a first order reaction was completed in 32 minutes when was 50% of the reaction completed **[AMU 1999; Kerala (Med.) 2003]**

(a) 16 *min.* (b) 24 *min.*

(c) 8 *min.* (d) 4 *min.*

145. The decomposition of N_2O_5 occurs as, $2N_2O_5 \rightarrow 4NO_2 + O_2$, and follows I^st^ order kinetics, hence **[BVP 2003]**

(a) The reaction is unimolecular

(b) The reaction is bimolecular

(c) $T_{1/2} \propto a^0$

(d) None of these

146. Which equation is correct for first order reactions **[MP PMT 2003]**

(a) $t_{1/2} \propto C^{-1}$ (b) $t_{1/2} \propto C$

(c) $t_{1/2} \propto C^0$ (d) $t_{1/2} \propto C^{1/2}$

147. For the reaction system $2NO(g) + O_2(g) \rightarrow 2NO_2(g)$ volume is suddenly produced to half its value by increasing the pressure on it. If the reaction is of first order with respect to O_2 and second order with respect to NO, the rate of reaction will **[AIEEE 2003]**

(a) Diminish to one fourth of its initial value

(b) Diminish to one eighth of its initial value

(c) Increase to eight times of its initial value

(d) Increase to four times of its initial value

148. If the rate of the reaction is equal to the rate constant, the order of the reaction is **[CBSE PMT 2003]**

(a) 3 (b) 0

(c) 1 (d) 2

149. The reaction $A \rightarrow B$ follows first order kinetics. The time taken for 0.8 mole of *A* to produce 0.6 mole of *B* is 1 *hour*. What is the time taken for conversion of 0.9 mole of *A* to produce 0.675 mole of *B* **[CBSE PMT 2003]**

(a) 2 *hours* (b) 1 *hour*

(c) 0.5 *hour* (d) 0.25 *hour*

150. The unit of velocity constant in case of zero order reaction is **[MP PMT 2004]**

(a) $\text{Concentration} \times \text{Time}^{-1}$ (b) $\text{Concentration}^{-1} \times \text{Time}^{-1}$

(c) $\text{Concentration} \times \text{Time}^{2}$ (d) $\text{Concentration}^{-1} \times \text{Time}$

151. Which one of the following is wrongly matched **[KCET 2004]**

(a) Saponification of $CH_3COOC_2H_5$ – Second order reaction

(b) Hydrolysis of CH_3COOCH_3 – Pseudo uni-molecular reaction

(c) Decomposition of H_2O_2 – First order reaction

(d) Combination of H_2 and Br_2 to give HBr – Zero order reaction

152. Which of the following is an example of pseudo unimolecular reaction **[Pb. CET 2001]**

(a) $CH_3COOCH_3 + H_2O \xrightarrow{H^+} CH_3COOH + CH_3OH$

(b) $CH_3COOCH_3 + H_2O \xrightarrow{OH^-} CH_3COOH + CH_3OH$

(c) $2FeCl_3 + SnCl_2 \rightarrow SnCl_4 + 2FeCl_2$

(d) $NaOH + HCl \rightarrow NaCl + H_2O$

153. Hydrolysis of DDT is a first order reaction, its half life is 10 years. Time to hydrolyse 10 *g* DDT to half is **[BVP 2004]**

(a) 100 years (b) 50 years

(c) 5 years (d) 10 years

154. In a first order reaction, the concentration of the reactant, decreases from 0.8 *M* to 0.4 *M* in 15 minutes. The time taken for the concentration to change from 0.1 *M* to 0.025 *M* is **[AIEEE 2004]**

(a) 7.5 minutes (b) 15 minutes

(c) 30 minutes (d) 60 minutes

155. In the first order reaction, the concentration of the reactant is reduced to 25% in one hour. The half life period of the reaction is **[DCE 2004]**

(a) 2 *hr* (b) 4 *hr*

(c) 1/2 *hr* (d) 1/4 *hr*

156. For a reaction, $X(g) \rightarrow Y(g) + Z(g)$ the half life period is 10 min. In What period of time would the concentration of *X* be reduced to 10% of original concentration **[DCE 2004]**

(a) 20 *min* (b) 33 *min*

(c) 15 *min* (d) 25 *min*

157. A first order reaction with respect to the reactant *A* has a rate constant of $6\ \sec^{-1}$. If we start with [*A*] = 0.5 mol/litre, then in what time the concentration of *A* becomes 0.05 mol/litre

[DCE 2004]

(a) 0.384 *sec* (b) 0.214 *sec*

(c) 3.84 *sec* (d) 0.402 *sec*

158. Order of radioactive disintegration reaction is

[JEE Orissa 2004]

(a) Zero (b) First

(c) Second (d) Third

159. The rate of a first order reaction is $1.5 \times 10^{-2}\ mol L^{-1}\ \min^{-1}$ at 0.5 *M* concentration of the reactant. The half life of the reaction is **[CBSE PMT 2004]**

(a) 8.73 *min* (b) 7.53 *min*

(c) 0.383 *min* (d) 23.1 *min*

160. A first order reaction was started with a decimolar solution of the reactant, 8 minutes and 20 seconds later its concentration was found to be $M/100$. So the rate of the reaction is **[Kerala PMT 2004]**

(a) $2.303 \times 10^{-5}\ \sec^{-1}$ (b) $2.303 \times 10^{-4}\ \sec^{-1}$

(c) $4.606 \times 10^{-3}\ \sec^{-1}$ (d) $2.606 \times 10^{-5}\ \sec^{-1}$

(e) $2.603 \times 10^{-4}\ \sec^{-1}$

161. Which is correct about zero order reaction

[JEE Orissa 2004]

(a) Rate of reaction depends on decay constant

(b) Rate of reaction is independent of concentration

(c) Unit of rate constant is concentration^{-1}

(d) Unit of rate constant is concentration^{-1} time^{-1}

162. Decay of ${}_{92}U^{235}$ is .....order reaction **[JEE Orissa 2004]**

(a) Zero (b) First

(c) Second (d) Third

163. The half-life of 2 sample are 0.1 and 0.4 seconds. Their respective concentration are 200 and 50 respectively. What is the order of the reaction **[JEE Orissa 2004]**

(a) 0 (b) 2

(c) 1 (d) 4

164. The following statements(s) is(are) correct **[IIT 1999]**

(a) A plot of $\log K_p$ *versus* $1/T$ is linear

(b) A plot of $\log[X]$ *versus* time is linear for a first order reaction $X \rightarrow P$

(c) A plot of $\log P$ *versus* $1/T$ is linear at constant volume

(d) A plot of P *versus* $1/V$ is linear at constant temperature

165. For a first order reaction **[IIT 1998]**

(a) The degree of dissociation is equal to $(1 - e^{-kt})$

(b) A plot of reciprocal concentration of the reactant *vs* time gives a straight line

(c) The time taken for the completion of 75% reaction is thrice the $t_{1/2}$ of the reaction

(d) The pre-exponential factor in the Arrhenius equation has the dimension of time T^{-1}

166. For reaction a $A \rightarrow xP$, when $[A] = 2.2\,mM$, the rate was found to be $2.4\,mM\,s^{-1}$. On reducing concentration of *A* to half, the rate changes to $0.6\,mM\,s^{-1}$. The order of reaction with respect to *A* is **[AIIMS 2005]**

(a) 1.5 (b) 2.0

(c) 2.5 (d) 3.0

167. Which one of the following statement for order of reaction is not correct **[IIT 2005]**

(a) Order can be determined experimentally.

(b) Order of reaction is equal to sum of the powers of concentration terms in differential rate law.

(c) It is not affected with the stoichiometric coefficient of the reactants.

(d) Order cannot be fractional.

168. $t_{\frac{1}{4}}$ can be taken as the time taken for the concentration of a reactant to drop to $\frac{3}{4}$ of its initial value. If the rate constant for a first order reaction is K, the $t_{\frac{1}{4}}$ can be written as

[AIEEE 2005]

(a) $0.10 / K$ (b) $0.29 / K$

(c) $0.69 / K$ (d) $0.75 / K$

169. For a first order reaction $A \rightarrow B$ the reaction rate at reactant concentration of $0.01M$ is found to be $2.0 \times 10^{-5} mol\ L^{-1} s^{1}$. The half life period of the reaction is

[CBSE PMT 2005]

(a) 220 *s* (b) 30 *s*

(c) 300 *s* (d) 347 *s*

170. The rate of reaction between two reactants *A* and *B* decreases by a factor of 4 if the concentration of reactant B is doubled. The order of this reaction with respect to reactant *B* is **[CBSE PMT 2005]**

(a) – 1 (b) – 2

(c) 1 (d) 2

171. If a substance with half life 3 days is taken at other place in 12 days. What amount of substance is left now **[AFMC 2005]**

(a) 1/4 (b) 1/8

(c) 1/16 (d) 1/32

172. The half-life of a first order reaction having rate constant $K = 1.7 \times 10^{-5}\ s^{-1}$ is

[BHU 2005]

(a) 12.1 *h* (b) 9.7 *h*

(c) 11.3 *h* (d) 1.8 *h*

173. For the reaction $A + B \rightarrow C$, it is found that doubling the concentration of *A* increases the rate by 4 times, and doubling the concentration of *B* doubles the reaction rate. What is the overal order of the reaction.

[KCET 2005]

(a) 4 (b) 3/2

(c) 3 (d) 1

174. Which of the following reactions end in finite time

[DPMT 2005]

(a) 0 order (b) 1st order

(c) 2nd order (d) 3rd order

Collision theory, Energy of activation and Arrhenius equation

1. A large increase in the rate of a reaction for a rise in temperature is due to **[EAMCET 1980; MP PET 1995]**

(a) The decrease in the number of collisions

(b) The increase in the number of activated molecules

(c) The shortening of the mean free path

(d) The lowering of the activation energy

2. Which of the following statements is not true according to collision theory of reaction rates

(a) Collision of molecules is a precondition for any reaction to occur

(b) All collisions result in the formation of the products

(c) Only activated collisions result in the formation of the products

(d) Molecules which have acquired the energy of activation can collide effectively

3. According to the collision theory of chemical reactions

(a) A chemical reaction occurs with every molecular collision

(b) Rate is directly proportional to the number of collisions per second

(c) Reactions in the gas phase are always of zero order

(d) Reaction rates are of the order of molecular speeds

4. According to the collision theory of reaction rates, rate of reaction increases with temperature due to

(a) Greater number of collisions

(b) Greater velocity of the reacting molecules

(c) Greater number of molecules have activation energy

(d) None of the above

5. The reaction rate at a given temperature becomes slower, then

[MP PMT 1993; DPMT 2000]

(a) The free energy of activation is higher

(b) The free energy of activation is lower

(c) The entropy changes

(d) The initial concentration of the reactants remains constant

6. A rise in temperature increases the velocity of a reaction. It is because it results in

(a) An increased number of molecular collisions

(b) An increased momentum of colliding molecules

(c) An increase in the activation energy

(d) A decrease in the activation energy

7. The number of collisions depend upon

(a) Pressure (b) Concentration

(c) Temperature (d) All the above

8. If E_f and E_r are the activation energies of forward and reverse reactions and the reaction is known to be exothermic, then

(a) $E_f > E_r$

(b) $E_f < E_r$

(c) $E_f = E_r$

(d) No relation can be given between E_f and E_r as data are not sufficient

9. According to Arrhenius theory, the activation energy is

(a) The energy it should possess so that it can enter into an effective collision

(b) The energy which the molecule should possess in order to undergo reaction

(c) The energy it has to acquire further so that it can enter into a effective collison

(d) The energy gained by the molecules on colliding with another molecule

10. The energy of activation is

(a) The energy associated with the activated molecules

(b) Threshold energy – energy of normal molecules

(c) Threshold energy + energy of normal molecules

(d) Energy of products – energy of reactants

11. Which one of the following does not represent Arrhenius equation

(a) $k = Ae^{-E/RT}$

(b) $\log_e k = \log_e A - \frac{E}{RT}$

(c) $\log_{10} k = \log_{10} A - \frac{E}{2.303RT}$

(d) $k = AE^{-RT}$

12. On increasing the temperature, the rate of the reaction increases because of

[MP PMT 1997]

(a) Decrease in the number of collisions

(b) Decrease in the energy of activation

(c) Decrease in the number of activated molecules

(d) Increase in the number of effective collisions

13. Energy of activation of a reactant is reduced by

(a) Increased temperature (b) Reduced temperature

(c) Reduced pressure (d) Increased pressure

14. The minimum energy a molecule should possess in order to enter into a fruitful collision is known as

[Kurukshetra CEE 2002]

(a) Reaction energy (b) Collision energy

(c) Activation energy (d) Threshold energy

15. Activation energy is

(a) The amount of energy to be added to the actual energy of a molecule so that the threshold energy is reached

(b) The amount of energy the molecule must contain so that it reacts

(c) The energy which a molecule should have in order to enter into an effective collision

(d) The average kinetic energy of the molecule

16. The reason for almost doubling the rate of reaction on increasing the temperature of the reaction system by 10^{oC} is

[J & K 2005]

(a) The value of threshold energy increases

(b) Collision frequency increases

(c) The fraction of the molecule having energy equal to threshold energy or more increases

(d) Activation energy decreases

17. The activation energy for a simple chemical reaction $A \rightarrow B$ is E_a in forward direction. The activation energy for reverse reaction **[CBSE PMT 2003]**

(a) Is always double of E_a

(b) Is negative of E_a

(c) Is always less than E_a

(d) Can be less than or more than E_a

18. Arrhenius equation is

(a) $\frac{d\ln K}{dT} = \Delta E^* / RT$ (b) $\frac{d\ln K}{dT} = \Delta E^* / RT^2$

(c) $\frac{d\ln K}{dT} = -\Delta E^* / RT^2$ (d) $\frac{d\ln K}{dT} = -\Delta E^* / RT$

19. Activation energy of any reaction depends on

(a) Temperature

(b) Nature of reactants

(c) Number of collisions per unit time

(d) Concentration of reactants

20. Relation between rate constant and temperature by Arrhenius equation is

(a) $\log_e A = \log_e K + \frac{E_a}{RT}$ (b) $\log K = A\frac{E_a}{RT}$

(c) $\log_e K = \log_e A - \frac{E_a}{RT^2}$ (d) $\log A = RT\ln E_a - \ln K$

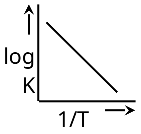
21. An endothermic reaction $A \to B$ has an activation energy $15 kcal/mole$ and energy of reaction $5 kcal/mole$. The activation energy of the reaction $B \to A$ is **[Pb. CET 1985]**

(a) 20 *kcal/mole* (b) 15 *kcal/mole*

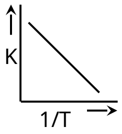
(c) 10 *kcal/mole* (d) None of these

22. Which of the following plots is in accordance with the Arrhenius equation

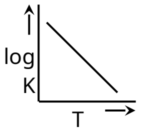
(a)



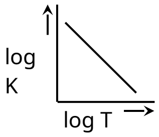
(b)



(c)



(d)



23. The Arrhenius equation expressing the effect of temperature on the rate constant of a reaction is **[MP PET 1997]**

(a) $k = e^{-E_a/RT}$ (b) $k = E_a / RT$

(c) $k = \log_e \frac{E_a}{RT}$ (d) $k = Ae^{-E_a/RT}$

24. For a reaction, activation energy $(E_a) = 0$ and rate constant $(K) = 3.2 \times 10^6 s^{-1}$ at 300 *K*. What is the value of the rate constant at 310 *K* **[KCET (Med.) 1999]**

(a) $3.2 \times 10^{-12} s^{-1}$ (b) $3.2 \times 10^6 s^{-1}$

(c) $6.4 \times 10^{12} s^{-1}$ (d) $6.4 \times 10^6 s^{-1}$

25. Activation energy is given by the formula **[DCE 1999]**

(a) $\log\frac{K_2}{K_1} = \frac{E_a}{2.303R}\left[\frac{T_2 - T_1}{T_1 T_2}\right]$

(b) $\log\frac{K_1}{K_2} = -\frac{E_a}{2.303R}\left[\frac{T_2 - T_1}{T_1 T_2}\right]$

(c) $\log\frac{K_1}{K_2} = -\frac{E_a}{2.303R}\left[\frac{T_1 - T_2}{T_1 T_2}\right]$

(d) None of these

26. A reaction having equal activation energies for forward and reverse reaction has **[MP PMT 2002]**

(a) $\Delta H = 0$ (b) $\Delta S = 0$

(c) Zero order (d) None of these

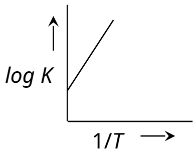
27. Collision theory is applicable to **[MP PMT 2002]**

(a) First order reactions (b) Zero order reactions

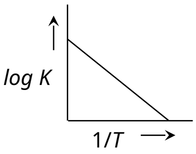
(c) Bimolecular reactions (d) Intra molecular reactions

28. A graph plotted between log *K* vs 1/*T* for calculating activation energy is shown by **[MP PET 2002]**

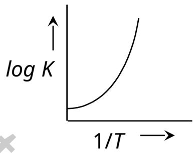
(a)



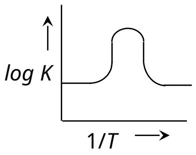
(b)



(c)



(d)



29. The rate constant of a reaction at temperature 200*K* is 10 times less than the rate constant at 400 *K*. What is the activation energy (E_a) of the reaction (*R* = gas constant)

[EAMCET 2003]

(a) 1842.4 *R* (b) 921.2 *R*

(c) 460.6 *R* (d) 230.3 *R*

30. In respect of the equation $k = Ae^{-E_a/RT}$ in chemical kinetics, which one of the following statement is correct

[AIEEE 2003]

(a) *k* is equilibrium constant

(b) *A* is adsorption factor

(c) E_a is energy of activation

(d) *R* is Rydberg's constant

31. The rate constant is doubled when temperature increases from 27°*C* to 37°*C*. Activation energy in *kJ* is

[JEE Orissa 2004]

(a) 34 (b) 54

(c) 100 (d) 50

32. The activation energy of a reaction is zero. The rate constant of this reaction

(a) Increases with increase of temperature

(b) Decreases with an increase of temperature

(c) Decreases with decrease of temperature

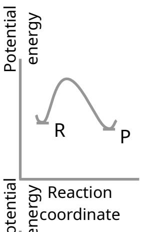
(d) Is independent of temperature

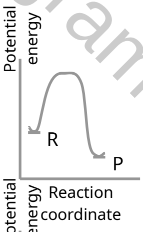
33. The rate constant is given by the equation $k = pze^{-E/RT}$. Which factor should register a decrease for the reaction to proceed more rapidly **[MP PET/PMT 1998]**

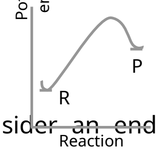
(a) T (b) Z

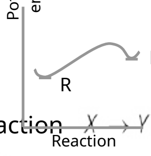
(c) E (d) p

34. An endothermic reaction with high activation energy for the forward reaction is given by the diagram: **[AIIMS 2005]**

(a)


(b)


(c)


(d)


35. Consider an endothermic reaction $X \to Y$ with the activation energies E_b and E_f for the backward and forward reactions, respectively, in general **[AIEEE 2005]**

(a) $E_b < E_f$

(b) $E_b > E_f$

(c) $E_b = E_f$

(d) There is no definite relation between E_b and E_f

36. Temperature dependent equation can be written as **[Orrisa JEE 2005]**

(a) $\ln k = \ln A - e^{E_a/RT}$ (b) $\ln k = \ln A + e^{E_a/RT}$

(c) $\ln k = \ln A - e^{RT/E_a}$ (d) All of these

Photochemical reactions

1. The formation of starch in plants results from

(a) Photosynthesis (b) Photolysis

(c) Flash photolysis (d) None of the above

2. The photolysis of water gives the substance

(a) $OH^- + H^+$ (b) $H_2 + OH^-$

(c) $H_2 + O_2$ (d) $H_2O + H_2O_2$

3. The law of photochemical equivalence was given by

(a) Drapper (b) Grauths

(c) Einstein (d) Labbert

4. If *'I'* is the intensity of absorbed light and *C* is the concentration of *AB* for the photochemical process $AB + h\nu \to AB^*$, the rate of formation of *AB** is directly proportional to **[IIT Screening 2001]**

(a) C (b) I

(c) I^2 (d) $C.I$

Critical Thinking

Objective Questions

1. For the reaction $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$, the rate of reaction is expressed as **[CBSE PMT 1997; AIEEE 2002]**

(a) $-\frac{\Delta[I_2]}{\Delta t} = -\frac{\Delta[H_2]}{\Delta t} = \frac{1}{2}\frac{\Delta[HI]}{\Delta t}$

(b) $\frac{\Delta[I_2]}{\Delta t} = \frac{\Delta[H_2]}{\Delta t} = \frac{\Delta[HI]}{2\Delta t}$

(c) $\frac{\Delta[H_2]}{\Delta t} = \frac{1}{2}\frac{\Delta[I_2]}{\Delta t} = -\frac{\Delta[HI]}{\Delta t}$

(d) None of these

2. If $3A \to 2B$, then the rate of reaction of $+\frac{d(B)}{dt}$ is equal to **[CBSE PMT 2002]**

(a) $+2\frac{d(A)}{dt}$ (b) $-\frac{1}{3}\frac{d(A)}{dt}$

(c) $-\frac{2}{3}\frac{d(A)}{dt}$ (d) $-\frac{3}{2}\frac{d(A)}{dt}$

3. The differential rate law for the reaction $H_2 + I_2 \to 2HI$ is **[AIEEE 2002]**

(a) $-\frac{d[H_2]}{dt} = -\frac{d[I_2]}{dt} = +\frac{1}{2}\frac{d[HI]}{dt}$

(b) $\frac{d[H_2]}{dt} = \frac{d[HI]}{dt} = \frac{1}{2}\frac{d[HI]}{dt}$

(c) $\frac{1}{2}\frac{d[H_2]}{dt} = \frac{1}{2}\frac{d[I_2]}{dt} = -\frac{d[HI]}{dt}$

(d) $-2\frac{d[H_2]}{dt} = -2\frac{d[I_2]}{dt} = +\frac{d[HI]}{dt}$

4. The rate law for a reaction between the substances *A* and *B* is given by, rate $= k[A]^n[B]^m$. On doubling the concentration of *A* and halving the concentration of *B*, the ratio of the new rate to the earlier rate of the reaction will be as **[AIEEE 2003]**

(a) $\frac{1}{2^{(m+n)}}$
(b) $(m+n)$
(c) $(n-m)$
(d) $2^{(n-m)}$

5. If we plot a graph between log *K* and $\frac{1}{T}$ by Arrhenius equation, the slope is **[UPSEAT 2001]**

(a) $-\frac{E_a}{R}$
(b) $+\frac{E_a}{R}$
(c) $-\frac{E_a}{2.303R}$
(d) $+\frac{E_a}{2.303R}$

6. For an endothermic reaction, where ΔH represents the enthalpy of the reaction in $kJ\ /mol$, the minimum value for the energy of activation will be **[IIT 1992]**

(a) Less than ΔH
(b) Zero
(c) More than ΔH
(d) Equal to ΔH

7. The rate constant (K') of one reaction is double of the rate constant (K'') of another reaction. Then the relationship between the corresponding activation energies of the two reactions (E_a' and E_a'') will be **[MP PET 1994; UPSEAT 2001]**

(a) $E_a' > E_a''$
(b) $E_a' = E_a''$
(c) $E_a' < E_a''$
(d) $E_a' = 4E_a''$

8. The rate constant, the activation energy and the arrhenius parameter of a chemical reaction at 25^0C are $3.0 \times 10^{-4} s^{-1}$, $104.4 kJ\ mol^{-1}$ and $6.0 \times 10^{14} s^{-1}$ respectively. The value of the rate constant as $T \to \infty$ is **[IIT 1996]**

(a) $2.0 \times 10^{18} s^{-1}$
(b) $6.0 \times 10^{14} s^{-1}$
(c) Infinity
(d) $3.6 \times 10^{30} s^{-1}$

9. The ΔH value of the reaction $H_2 + Cl_2 \rightleftharpoons 2HCl$ is $-44.12 kcal$. If E_1 is the activation energy of the products, then for the above reaction **[EAMCET 1997]**

(a) $E_1 > E_2$
(b) $E_1 < E_2$
(c) $E_1 = E_2$
(d) ΔH is not related to E_1 and E_2
(e) None is correct

10. The temperature dependence of rate constant (k) of a chemical reaction is written in terms of Arrhenius equation, $K = A.e^{-E^*/RT}$. Activation energy (E^*) of the reaction can be calculated by plotting **[CBSE PMT 2003]**

(a) $\log k \ vs \ \frac{1}{\log T}$
(b) $k \ vs \ T$
(c) $k \ vs \ \frac{1}{\log T}$
(d) $\log k \ vs \ \frac{1}{T}$

11. Activation energy of a chemical reaction can be determined by **[CBSE PMT 1998; AFMC 1999; BHU 2000]**

(a) Changing concentration of reactants
(b) Evaluating rate constant at standard temperature
(c) Evaluating rate constants at two different temperatures
(d) Evaluating velocities of reaction at two different temperatures

12. The activation energy for a reaction is $9.0\ K\ cal/mol$. The increase in the rate constant when its temperature is increased from 298*K* to 308*K* is **[JIPMER 2000]**

(a) 63%
(b) 50%
(c) 100%
(d) 10%

13. Which of the following is the fastest reaction **[Pb. CET 2002]**

(a) $C + \frac{1}{2}O_2 \xrightarrow{250^\circ C} CO$
(b) $C + \frac{1}{2}O_2 \xrightarrow{500^\circ C} CO$
(c) $C + \frac{1}{2}O_2 \xrightarrow{750^\circ C} CO$
(d) $C + \frac{1}{2}O_2 \xrightarrow{1000^\circ C} CO$

14. The rate constant *k,* for the reaction $N_2O_5(g) \to 2NO_2(g) + \frac{1}{2}O_2(g)$ is $2.3 \times 10^{-2} s^{-1}$. Which equation given below describes the change of $[N_2O_5]$ with time? $[N_2O_5]_0$ and $[N_2O_5]_t$ correspond to concentration of N_2O_5 initially and at time, *t* **[AIIMS 2004]**

(a) $[N_2O_5]_t = [N_2O_5]_0 + kt$
(b) $[N_2O_5]_0 = [N_2O_5]_t e^{kt}$
(c) $\log_{10}[N_2O_5]_t = \log_{10}[N_2O_5]_0 - kt$
(d) $\text{In}\frac{[N_2O_5]_0}{[N_2O_5]_t} = kt$

15. For the reaction $CH_3COOCH_3 + H_2O \xrightarrow{H^+} CH_3COOH + CH_3OH$ The progress of the process of reaction is followed by

(a) Finding the amount of methanol formed at different intervals

(b) Finding the amount of acetic acid formed at different intervals

(c) Using a voltmeter

(d) Using a polarimeter

16. Half life of a reaction is found to be inversely proportional to the cube of its initial concentration. The order of reaction is

[KCET 2002]

(a) 2 (b) 5

(c) 3 (d) 4

17. The integrated rate equation is $Rt = \log C_0 - \log C_t$. The straight line graph is obtained by plotting **[AIEEE 2002]**

(a) $\text{time v/s} \log C_t$ (b) $\frac{1}{\text{time}} \text{v/s}\ C_t$

(c) $\text{time v/s}\ C_t$ (d) $\frac{1}{\text{time}} \text{v/s} \frac{1}{C_t}$

18. For which order reaction a straight line is obtained along with *x*–axis by plotting a graph between half life $(t_{1/2})$ and initial concentration '*a*'

[RPET 2003]

(a) 1 (b) 2

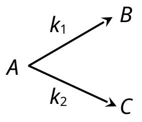
(c) 3 (d) 0

19. The reaction, $X \rightarrow$ product follows first order kinetics. In 40 minutes the concentration of *X* changes from 0.1 *M* to 0.025 *M* Then the rate of reaction when concentration of *X* is 0.01 *M*

(a) $1.73 \times 10^{-4}\ M\ \text{min}^{-1}$ (b) $3.47 \times 10^{-5}\ M\ \text{min}^{-1}$

(c) $3.47 \times 10^{-4}\ M\ \text{min}^{-1}$ (d) $1.73 \times 10^{-5}\ M\ \text{min}^{-1}$

20. A Substance undergoes first order decomposition. The decomposition follows two parallel first order reactions as



$k_1 = 1.26 \times 10^{-4}\ s^{-}$
1--------dfsfsfsf
$k_1 = 3.8 \times 10^{-5}\ s^{-}$
1--------dfsfsfsf

The percentage distribution of *B* and *C* are

[Kerala PMT 2004]

(a) 75% *B* and 25% *C* (b) 80% *B* and 20% *C*

(c) 60% *B* and 40% *C* (d) 90% *B* and 10% *C*

(e) 76.83% *B* and 23.17% *C*

AR Assertion & Reason

For AIIMS Aspirants

Read the assertion and reason carefully to mark the correct option out of the options given below :

(a) If both assertion and reason are true and the reason is the correct explanation of the assertion.

(b) If both assertion and reason are true but reason is not the correct explanation of the assertion.

(c) If assertion is true but reason is false.

(d) If the assertion and reason both are false.

(e) If assertion is false but reason is true.

1. Assertion : Instantaneous rate of reaction is equal to dx/dt.

Reason : It is the rate of reaction at any particular instant of time.

2. Assertion : Molecularity has no meaning for a complex reaction.

Reason : The overall molecularity of a complex reaction is equal to the molecularity of the slowest step.

3. Assertion : If in a zero order reaction, the concentration of the reactant is doubled, the half-life period is also doubled.

Reason : For a zero order reaction, the rate of reaction is independent of initial concentration.

4. Assertion : If the activation energy of a reaction is zero, temperature will have no effect on the rate constant.

Reason : Lower the activation energy, faster is the reaction.

5. Assertion : According to steady state hypothesis, in a multistep reaction, the change in concentration with time for reactive intermediates is zero.

Reason : The intermediates are so reactive that after a brief initial period their concentrations rise from zero to a small value and remains constant for most of the duration of the reaction.

6. Assertion : Half-life period of a reaction of first order is independent of initial concentration.

Reason : Half-life period for a first order reaction $t_{1/2} = \frac{2.303}{K}\log 2$.

7. Assertion : The photochemical reactions $H_2 + Cl_2 \rightarrow 2HCl$ and $H_2 + Br_2 \rightarrow 2HBr$ have equal quantum efficiencies.

Reason : Both the reactions proceed by similar mechanism.

8. Assertion : Vision is not a photochemical reaction.

Reason : Halogenation of alkenes is a photochemical reaction.

9. Assertion : Glow worm shows chemiluminescence.

Reason : Glow worm emits light due to oxidation of protein, luciferin present in it.

10. Assertion : The rate of reaction is always negative.

Reason : Minus sign used in expressing the rate shows that concentration of product is decreasing.

11. Assertion : The kinetic of the reaction $mA + nB + pC \rightarrow m'X + n'Y + p'Z$ obeys the rate expression as $\frac{dx}{dt} = k[A]^m[B]^n$.

Reason : The rate of the reaction does not depend upon the concentration of *C*.

Answers

Rate of a reaction

1	b	2	a	3	d	4	b	5	b
6	c	7	c	8	c	9	a	10	b
11	b	12	b	13	c	14	d	15	b
16	b	17	c	18	b	19	d	20	a
21	b	22	a	23	d	24	c	25	a
26	a	27	a	28	b	29	b	30	b
31	a	32	c	33	b	34	a	35	c
36	d	37	a	38	b	39	a	40	c
41	a	42	b						

Rate law and Rate constant

1	d	2	c	3	a	4	b	5	a
6	a	7	a	8	c	9	b	10	b
11	b	12	d	13	a	14	c	15	d
16	d	17	c	18	a	19	c	20	c
21	b	22	a	23	a	24	d	25	b
26	a	27	a	28	c	29	c	30	d
31	d	32	c	33	c	34	d	35	b
36	c	37	c	38	a	39	c	40	b
41	a	42	d	43	a	44	c	45	c
46	a	47	b	48	b	49	c	50	b
51	b	52	a	53	a	54	d	55	d
56	c	57	d	58	b	59	b	60	b
61	c	62	d	63	c	64	b	65	c
66	d	67	b	68	c	69	c	70	b
71	d	72	d	73	b	74	b	75	d
76	b	77	b	78	c	79	c	80	c
81	b	82	b	83	c	84	a	85	a
86	c	87	c	88	a	89	c	90	c
91	b	92	b	93	c	94	b	95	b
96	d	97	b	98	c	99	a	100	c
101	b	102	d	103	c	104	c	105	a
106	d	107	a	108	b	109	c	110	b
111	c	112	d	113	b	114	b	115	d
116	d	117	b	118	d	119	a	120	b
121	d	122	b	123	d	124	c	125	d
126	b	127	d	128	d	129	b	130	a
131	ac	132	c	133	d	134	c	135	a
136	a	137	c	138	c	139	d	140	c
141	c	142	c	143	c	144	a	145	c
146	c	147	c	148	b	149	b	150	a
151	d	152	a	153	d	154	c	155	c
156	b	157	a	158	b	159	d	160	c
161	b	162	b	163	b	164	abd	165	ad
166	b	167	d	168	b	169	d	170	b
171	c	172	c	173	c	174	a		

Collision theory, Energy of activation and Arrhenius equation

1	b	2	b	3	b	4	c	5	a
6	d	7	d	8	b	9	c	10	b
11	d	12	d	13	a	14	d	15	a
16	b	17	d	18	b	19	b	20	a
21	c	22	a	23	d	24	b	25	a
26	ab	27	c	28	b	29	b	30	c
31	b	32	d	33	c	34	c	35	a
36	a								

Photochemical reaction

1	a	2	a	3	c	4	b		

Critical Thinking Questions

1	a	2	c	3	a	4	d	5	c
6	c	7	c	8	b	9	a	10	d
11	c	12	a	13	d	14	d	15	b
16	d	17	a	18	b	19	c	20	e

Assertion & Reason

1	b	2	b	3	b	4	b	5	a
6	a	7	d	8	e	9	a	10	d
11	a								

AS Answers and Solutions

Rate of a reaction

1. (b) Rate of reaction continuously decreases with time.

2. (a) The rate of reaction depends upon conc. of reactant, surface area of reactant, temperature, presence of light and catalyst.

3. (d) According to law of mass action.

4. (b) $R = K[RCl]$, if [*RCl*] =1/2, then rate = *R*/2.

5. (b) $2^2 = 4,\ 3^2 = 9$

6. (c) The rate of chemical reaction ∝ The product of the molar conc. of the reactants (at constant *T*)

7. (c) Rate of reaction = $\frac{dx}{dt} = \left[\frac{0.2-0.1}{10}\right] = \frac{0.1}{10}$

$= 0.01\ mol\ dm^{-3}\ min^{-1}$

8. (c) As reaction progressing the concentration of the reactants decreases and the concentration of the product increases.

9. (a) $\frac{-d(N_2)}{dt} = -\frac{1}{3}\frac{d(H_2)}{dt} = \frac{1}{2}\frac{d(NH_3)}{dt}$ = $\frac{3}{2}\times 40\times 10^{-3}$

$= 60\times 10^{-3}$.

10. (b) Greater are the concentrations of the reactants, faster is the reaction. Conversely, as the concentrations of the reactants decreases, the rate of reaction also decreases.

11. (b) Ionic reactions are very fast reactions i.e. take place instantaneously.

12. (b) Rate = $K(A)^2(B)^1$ on doubling the active mass of *A* the rate of reaction increase 4 times.

13. (c) '*A*' will disappear at twice the rate at which '*B*' will decrease.

14. (d) When volume is reduced to $\frac{1}{4}$, concentrations become four times.

16. (b) $\frac{-dN_2}{dt} = \frac{-1}{3}\frac{dH_2}{dt} = \frac{1}{2}\frac{dNH_3}{dt}$

$\frac{dH_2}{dt} = \frac{3}{2}\times 0.001 = 0.0015 kg\, hr^{-1}$.

18. (b) $-\frac{dc}{dt}$ refers as decrease in concentration of the reactant with time.

19. (d) The rate of a reaction depends upon concentration of reactant.

20. (a) $-\frac{1}{3}\frac{d[A]}{dt} = -\frac{d[B]}{dt} = \frac{+d[C]}{dt} = \frac{+d(D)}{dt}$.

21. (b) $N_2 + 3H_2 \rightleftharpoons 2NH_3$

$\frac{-\Delta[N_2]}{\Delta t} = -\frac{1}{3}\frac{\Delta[H_2]}{\Delta t} = \frac{1}{2}\frac{\Delta[NH_3]}{\Delta t}$

$\therefore \frac{\Delta[H_2]}{\Delta t} = \frac{3}{2}\times\frac{\Delta[NH_3]}{\Delta t} = \frac{3}{2}\times 2\times 10^{-4}$

$= 3\times 10^{-4}\ mol\ litre^{-1} sec^{-1}$

22. (a) Increase in concentration of $B = 5\times 10^{-3} mol\ l^{-1}$ $Time = 10\ sec$

Rate of appearance of B = $\frac{\text{Increase of conc. B}}{\text{Time taken}}$

$= \frac{5\times 10^{-3} mol\ l^{-1}}{10\ sec} = 5\times 10^{-4} mol\ l^{-1}\ Sec^{-1}$

24. (c) The rate of formation of SO_3 is $1.28\times 10^{-3}\ g/sec$.

26. (a) $\frac{K_{t+10}}{K_t} = \frac{r_{t+10}}{r_t} = 2$; For an increase of temperature to 50^oC, *i.e.* 5 times, the rate increases by 2^5 times, *i.e.* 32 times.

28. (b) $\frac{K_{t+10}}{K_t} = \frac{r_{t+10}}{r_t} = 2$.

For an increase of temperature to $20^\circ C$ *i.e.* 2 times, the rate increase by 2^2 times, *i.e.* 4 times.

29. (b) $\frac{k_{t+10}}{K_t} = \frac{r_{t+10}}{r_t} = 2$

For an increase of temperature to 90^oC *i.e.* 9 times, the rate increases by 2^9 times *i.e.* 512.

30. (b) Catalyst increases the rate by decreasing the activation energy.

31. (a) For 10K rise in temperature, the rate of reaction nearly doubles.

32. (c) Temperature coefficient $\frac{K_{35^oC}}{K_{25^oC}} = \frac{K_{308k}}{K_{298k}} = 2$ and 3 for most reactions.

33. (b) Catalyst decrease energy of activation.

34. (a) Thus both rate and rate constant *K* increase with temperature, $r = k(\text{reactant})^n$ and $k = Ae^{-E_a/RT}$

35. (c) Enzymes does not always increase activation energy.

36. (d) Catalyst reduce the activation energy for reaction and thus increase the rate of reaction.

37. (a) Catalyst affect only activation energy. It brings down the activation energy of reaction.

38. (b) As we know that the velocity constant become double by increasing the temperature by 10°*C* so if at 290 K, velocity constant $= 3.2 \times 10^{-3}$ then at 300 *K*, velocity constant $= 2(K_{290})$ $= 2 \times 3.2 \times 10^{-3} = 6.4 \times 10^{-3}$.

39. (a) Higher the value of rate constant so, faster the reaction rate.

40. (c) Rate of reaction may increase or decrease with increase in temperature. If reaction is exothermic, rate decreases with increasing temperature while that of endothermic reactions increase with increasing temperature.

41. (a) $2N_2O_{5(g)} \rightarrow 4NO_{2(g)} + O_{2(g)}$

Rate of reaction with respect to NO_2

$$= \frac{1}{4}\frac{d[NO_2]}{dt} = \frac{1}{4} \times \frac{5.2 \times 10^{-3}}{100} = 1.3 \times 10^{-5} ms^{-}$$

42. (b) In first phase, $K = \frac{2.303}{20}\log\frac{90}{100}$ .....(i)

In second phase $K = \frac{2.303}{t}\log\frac{81}{100}$ .....(ii)

From eq. (i) $\frac{2.303}{20}\log\frac{90}{100} = \frac{2.303}{t}\log\frac{81}{100}$

$$t = \frac{20(\log 81 - \log 100)}{(\log 90 - \log 100)}$$

$= \frac{20(1.908 - 2)}{(1.954 - 2)} = \frac{20 \times (-0.092)}{(-0.046)}$ = 40 minutes

Rate law and Rate constant

1. (d) Molecularity of the reaction does not influence the rate of reaction.

2. (c) The rate law for an reaction can be given by; rate = $K(A)(B)^2$, *i.e.* the powers are raised which are given as coefficient of reactant.

3. (a) $p_0 = 500 atm$

$$K = \frac{2.303}{t}\log_{10}\frac{p_0}{p_t}$$

$$3.38 \times 10^{-5} = \frac{2.303}{10 \times 60}\log\frac{500}{p_t}$$

or $0.00880 = \log\frac{500}{p_t} \Rightarrow \frac{500}{1.02} = 490 atm$

4. (b) It is a pseudo-unimolecular reaction.

5. (a) $A + 2B \rightarrow C + D$

$$\frac{-d[A]}{dt} = 5 \times 10^{-4}$$

$$-\frac{1}{2}\frac{d[B]}{dt} = \frac{5 \times 10^{-4}}{2} = 2.5 \times 10^{-4} mol^{-1} \sec^{-1}$$

8. (c) For following reaction, $2NO_{(g)} + O_2(g) \rightarrow 2NO_2(g)$

When the volume of vessel change into $\frac{1}{3}$ then concentration of reactant become three times.

The rate of reaction for first order reaction $\propto$ concentration. So rate of reaction will increases three times.

9. (b) $2A + B \rightarrow$ Products

According to question : Rate of reaction of 'A' $\propto$ [B] as increase in rate is double when [B] is doubled.

Rate of reaction $\propto$ [A] [B] as increase in rate is 8 times when concentration of both reactant is doubled. It means that order of reaction is 3 and overall rate reaction should be $r = K[A]^2[B]$

10. (b) Let the rate of reaction depends on *x*th power of [*A*]. Then

$r_1 = k[A]^x$ and $r_2 = k[2A]^x$

$$\therefore \frac{r_1}{r_2} = \frac{[A]^x}{[2A]^x} = \frac{1}{4} = \left(\frac{1}{2}\right)^2 \quad (\because r_2 = 4r_1)$$

$\therefore x = 2$. As the reaction rate does not depend upon the concentration of B. Hence, the correct rate law will be rate $= K[A]^2[B]^o$ or $= K[A]^2$

11. (b) Velocity constant '*K*' is characteristic constant of a reaction and depends only on temperature and catalyst.

12. (d) Unit of *K* for Ist order reaction is $Time^{-1}$.

13. (a) $K = Ae^{-E_a/RT}$ by this equation it is clear that rate constant of a reaction depends on temperature

14. (c) $k = \frac{2.303}{t}\log_{10}\frac{a}{a-x}$;

$t = 2 \times 10^2, \; a = 800, \; a - x = 50$

$$k = \frac{2.303}{2\times10^2}\log_{10}\frac{800}{50} = \frac{2.303}{2\times10^2}\log_{10}16$$

$$= \frac{2.303}{2\times10^2}\log_{10}2^4 = \frac{2.303}{2\times10^4}\times4\times0.301$$

$$= 1.38\times10^{-2}\ s^{-1}$$

15. (d) Rate of reaction is quadrupled on doubling the concentration. Thus $r \propto [A]^2$.

16. (d) K is not constant for all the reaction.

19. (c) Rate determining step is a slow step by which rate of reaction can be determined.

20. (c) It is a second order reaction and the unit of k for second order reaction is *litre* $mol^{-1}\ sec^{-1}$.

21. (b) For reversible reaction rate constant is also reverse.

22. (a) Rate $= K(N_2O_5) = 6.2\times10^{-1}\times1.25$

$= 7.75\times10^{-1}\ mol\ l^{-1}\ s^{-1}$

23. (a) We know that for first order kinetics

$$k = \frac{2.303}{t}\log\frac{a}{a-x}$$

$(a-x) = 0.05\ mol\ l^{-1}$, $6 = \dfrac{2.303}{t}\log\dfrac{0.5}{0.05}$

or $t = \dfrac{2.303}{6}\log\dfrac{0.5}{0.05} = \dfrac{2.303}{6} = 0.384\min$

24. (d) Rate = $K(N_2O_5)$ hence

$2.4\times10^{-5} = 3.0\times10^{-5}(N_2O_5)$

or $(N_2O_5) = 0.8\ mol\ l^{-1}$

25. (b) $R = K[A]$,

$1.02\times10^{-4} = 3.4\times10^{-5},[N_2O_5]$

or $(N_2O_5) = \dfrac{1.02\times10^{-4}}{3.4\times10^{-5}}, K = 3$

26. (a) Rate law for the reaction

$2N_2O_5 \rightarrow 4NO_2 + O_2$

is $r = k[N_2O_5]$ first order reaction.

28. (c) Rate constant depends on temperature only.

29. (c) According to Arhenius concept

Rate constant $K = A_e^{-E_a/RT}$, Hence rate constant depends only upon temperature of the system.

30. (d) For $2A + B \rightarrow C$

Rate $= K[A][B]$

Value of rate constant $K = Ae^{-Ea/RT}$ here K is independent of the initial concentration of A and B.

31. (d) The specific rate constant of a first order reaction depends upon the temperature of reaction.

32. (c) Unit of K for first order reaction $= sec^{-1}$

35. (b) The rate of zero order reaction is not depend on the concentration of the reactants.

36. (c) The unit of K for zero order reaction

$= mole\ litre^{-1} sec^{-1}$.

37. (c) Order of reaction is sum of the power raised on concentration terms to express rate expression.

38. (a) The concentration of reactant does not change with time for zero order reaction (unit of K suggests zero order) since reactant is in excess.

39. (c) $r = K[A]^m$ also $2r = K[4A]^m$, $\dfrac{1}{2} = \left(\dfrac{1}{4}\right)^m$

$\therefore m = \dfrac{1}{2}$

40. (b) $K = \dfrac{2.303}{t}\log\dfrac{V_\infty}{V_\infty - V_t}$ gives constant value of K. With the given date. Hence it is 1st order.

42. (d) $r = K[A]^n,\quad 100r = K[10A]^n$

Thus $\dfrac{1}{100} = \left(\dfrac{1}{10}\right)^n$ or $n = 2$

43. (a) It is a standard example of first order because in that reaction rate of reaction affected by only one concentration term.

44. (c) Inversion of cane sugar is a Pseudo unimolecular reaction.

45. (c) For 1st order reaction

$$K = \frac{2.303}{t}\log_{10}\frac{a}{(a-x)}$$

46. (a) $t_{1/2} = \dfrac{0.693}{k} = \dfrac{0.693}{6.2\times10^{-4}} = 1117.7$ *sec.*

47. (b) $k = \dfrac{2.303}{t}\log\dfrac{a}{a-x}$

$\dfrac{0.693}{T} = \dfrac{2.303}{t}\log\dfrac{100}{100-30}$

$\therefore T = 58.2$ *min.*

48. (b) Order of reaction = $\dfrac{3}{2}+\dfrac{3}{2} = \dfrac{3+3}{2} = \dfrac{6}{2} = 3$

49. (c) Two molecules are taking part in elementary step.

50. (b) Because two molecules are taking part in elementary step.

51. (b) The overall order of a reaction is sum of powers T raised on concentration terms in order to write rate expression.

52. (a) It is a first order reaction as is clear from rate law expression, $r = k(H_2O_2)$

53. (a) For Ist order reaction half life is independent of concentration.

54. (d) $K=\frac{1}{t}\log e\left(\frac{a}{a-x}\right)=\frac{1}{15}\log e\left(\frac{35}{35-9}\right)$

$=\frac{1}{15}\log e\left(\frac{35}{26}\right)$

56. (c) $k=\frac{0.693}{30}=0.0231$;

$t=\frac{2.303}{k}\log\left(\frac{100}{100-75}\right)$

$t=\frac{2.303}{0.0231}\log 4=60\text{ minutes}$

57. (d) $Rate=K(sugar)(H_2O)^o$

58. (b) Derive $t_{1/2}$ from $K_t=2.303\log\frac{a}{a-x}$, putting $t=\frac{1}{2}$ and $x=\frac{a}{2}$. Therefore it is $\frac{0.693}{K}$.

59. (b) $r\propto[X]^2$ or $r=k[X]^2$

60. (b) $t_{1/2}=\frac{0.693}{k}, \frac{0.693}{1.1\times10^{-9}}=6.3\times10^{8}\ sec.$

61. (c) $t_{1/2}\propto\frac{1}{(a)}$ for II order reaction.

62. (d) Order of reaction is an experimental value, while molecularity is a theoretical value.

63. (c) *K* for 1st order reaction = per unit time *i.e.* $Time^{-1}$.

64. (b) $R=K[A][B]^0$ so molecularity is two and order is two.

65. (c) Rate of zero order reaction is independent of the concentration of the reactant and remains constant throughout the reaction.

66. (d) $t_{1/2}\propto\frac{1}{(a)^{n-1}}$

67. (b) $t_{1/2}\propto\frac{1}{(C_o)^{n-1}}$ ∴ reaction is of first order.

68. (c) For Ist order reaction half life is independent of concentration.

69. (c) $K=\frac{0.693}{t_{1/2}}, K=\frac{0.693}{138.6\text{ min}}=0.005\text{ min}^{-1}$

70. (b) $CH_3COOCH_3+H_2O\xrightarrow{H^+}CH_3COOH+CH_3OH$

It is a pseudo-unimolecular reaction.

71. (d) $t_{1/2}\propto\frac{1}{K}$ and $K\propto t$

73. (b) For zero order reactions $\frac{dx}{dt}=K(A)^o$

74. (b) It is an bimolecular and second order reaction.

75. (d) $\frac{dx}{dt}=(HI)^2$, then order of reaction = 2

76. (b) Rate = $K(\text{Sucrose})(H_2O)^o$

77. (b) Because in this reaction one molecule of N_2O_5 is used.

78. (c) Integrated velocity equation for first order reaction is: $k=\frac{2.303}{t}\log\frac{(A)_o}{(A)}$

80. (c) $t_{1/2}=\frac{2.303\log 2}{K}=\frac{0.693}{K}$

81. (b) Inversion of sugar is a pseudo-unimolecular reaction.

82. (b) For Ist order reaction

$\log(a-x)=\log a-\frac{kt}{2.303}$

$y=c+mx$

83. (c) $t_{1/2}=\frac{0.693}{k}=\frac{0.693}{3.46\times10^{-3}}=200min$

84. (a)

$\frac{1}{Time}\times(conc.)=\frac{moles\ l^{-1}}{Time}=moles\ l^{-1}time^{-1}$

for zero order reaction.

85. (a) The order of reaction is $\frac{3}{2}$ and molecularity is 2.

87. (c) Molecularity can never be fractional.

88. (a) As doubling the initial conc. doubles the rate of reaction, order = 1.

89. (c) When *B* is in excess, it becomes a pseudo-unimolecular reaction.

90. (c) $k=\frac{0.693}{t_{1/2}}=\frac{0.693}{69.35}=9.99\times10^{-3}=0.01s^{-1}$

91. (b) $k=\frac{0.693}{24}hr^{-1}=\frac{2.303}{96}\log\frac{10}{a-x}$

or $\log\frac{10}{a-x}=1.2036$ or 1 – log (*a* – *x*) = 1.2036

or $\log(a-x)=-0.2036=1.7964$

or $(a-x)=\text{antilog}1.7964=0.6258gm$

92. (b) $0.08\ mol\ l^{-1}$ to $0.01\ mol\ l^{-1}$ involves 3 half-life. So the t is 30 minutes

93. (c) $t_{1/2}$ of II order reaction is inversely proportional to initial concentration of reactants.

94. (b) As $r=k(H_2O_2)$, it is a reaction of 1st order.

97. (b) $r=k(C_A)^{3/2}(C_B)^{-1/2}$

Order = $\frac{3}{2}+\left(-\frac{1}{2}\right)=\frac{2}{2}=1$

98. (c) If rate $= K(A)^m(B)^n$, then order of reaction $= m+n$.

99. (a) $k=\frac{0.693}{t_{1/2}}=\frac{0.693}{100\text{ sec}}=6.93\times10^{-3}sec^{-1}$

100. (c) $t_{1/2}=\frac{0.693}{k}$

101. (b) $t_{1/2}=\frac{0.693}{k}$, $k=\frac{0.693}{480}=1.44\times10^{-3}\text{ sec}^{-1}$.

102. (d) $r=k(A)^2$, when concentration is doubled

$r=k(2A)^2=k\,4(A)^2$ the rate becomes 4 times.

103 (c) $r=K[FeCl_3]^2[SnCl_2]^1$. Order $=2+1=3$

105. (a) $t_{1/2}$ for I order reaction independent of initial concentration.

107. (a) The rate will be given by slowest step. Thus $r=K[A][B_2]$. $K_c=\frac{[A][A]}{[A_2]}$ or

$[A]=[K_c]^{1/2}[A_2]^{1/2}$

$r=K\times[K_c]^{1/2}[A_2]^{1/2}[B_2]=K[A_2]^{1/2}[B]$.

Thus order is $0.5+1=1.5$

108. (b) For Ist order reaction half life is independent of concentration.

110. (b) Rate = $K[A]^{1/2}[B]^{3/2}$

$\therefore O.R.=\frac{1}{2}+\frac{3}{2}=\frac{4}{2}=2$

112. (d) The rate of this photochemical reaction is independent of the concentration, therefore, it is zero order reaction.

113. (b) $t_{1/2}=\frac{0.693}{k}=\frac{0.693}{0.6932\ hr^{-1}}=1\ hr$.

114. (b) The unit of rate constant shows that reaction is of first order. For first order reaction, half life is independent of initial conc. of the reactant. Thus,

$t_{1/2}=\frac{0.693}{0.69\times10^{-1}}=\frac{0.693\times60}{0.69\times10^{-1}}=600\text{sec}$

115. (d) *Given* : Rate constant of the first order reaction $(K)=3\times10^{-6}$ per sec and initial concentration $[A]=0.10M$. We know that initial rate constant $K[A]=3\times10^{-6}\times0.10=3\times10^{-7}ms^{-1}$.

116. (d) It is the characteristic of pseudo-unimolecular reactions.

117. (b) It is a second order reaction.

118. (d) $r=K$ [reactant]

$\therefore K=\frac{1.0\times10^{-2}}{0.2}=0.05$

$t_{1/2}=\frac{0.693}{0.05}=13.86\,s$

119. (a) For first order reactions rate is depend on the concentration of one reactant.

120. (b) Molecularity of a reaction never become zero or fraction.

121. (d) $t=\frac{2.303}{k}\log\frac{a}{a-x}$

$t=\frac{2.303}{1.155\times10^{-3}}\log\frac{100}{100-50}=600\text{ sec}$

122. (b) Rate = $K[A]^{3/2}[B]^{-1}$

$\therefore O.R.=\frac{3}{2}+(-1)=\frac{1}{2}$

123. (d) $t_{1/2}\propto(CO)^o$ *i.e.* half life for Ist order is independent of initial concentration.

124. (c) $2NO_{(g)}+Cl_{2(g)}\rightarrow 2NOCl_{(g)}$

Rate = $K[NO]^2[Cl_2]^1$, $\therefore O.R.=2+1=3$

125. (d) $8\times10^{-5}=\frac{1}{t}\left[\frac{1}{0.5}-\frac{1}{1}\right]$; $8\times10^{-5}=\frac{1}{t}[2-1]$

$t=\frac{1}{8\times10^{-5}}=0.125\times10^5=1.25\times10^4\,min.$

126. (b) $r=k[\text{reactant}]^1$ $\therefore k=\frac{0.693\times10^{-2}}{1}$ also

$t_{1/2}=\frac{0.693}{k}=\frac{0.693}{0.693\times10^{-2}}=100\,\text{min}.$

127. (d) $t_{1/2}=\frac{1}{Ka}$ for second order reactions.

128. (d) $k=\frac{2.303}{t}\log\left(\frac{a}{a-x}\right)$;

$k=\frac{2.303}{30}\log\left(\frac{100}{100-75}\right)$

$k=\frac{2.303}{t}\log\left(\frac{100}{100-93.75}\right)$ Put the value of K from above equation we get the value of t therefore $\therefore$ $t=60\,\text{min}.$

129. (b) $k=\frac{0.693}{45}\text{min}^{-1}=\frac{2.303}{t_{99.9\%}}\log\frac{a}{a-0.999a}$ or

$t_{99.9\%}=\frac{2.303\times45}{0.693}\log10^3=448\text{ min}\approx7.5\ hrs$

130. (a) Given A(a) = 2.00 *m*, t = 200 *min* and a(a-x) = 0.15 *m* we know

$$k = \frac{2.303}{t}\log\frac{a}{a-x} = \frac{2.303}{200}\log\frac{2.00}{0.15}$$

$$= \frac{2.303}{200}\times(0.301+0.824) = 1.29\times10^{-2}\ \text{min}^{-1}$$

131. (a,c) The unit for zero order reaction is $mol\ litre^{-1}time^{-1}$

132. (c) It is a third order reaction because

$\text{Rate} = K[NO]^2[O_2]^1 \quad \therefore O.R. = 2+1 = 3$

133. (d) Order of a reaction is decided by relative concentration of reactants.

134. (c) Unit of rate constant for second order reaction is $mol^{-1}litre\ time^{-1}$

135. (a) $R = K[A]^2[B]$ order of reaction $= 2+1 = 3$

136. (a) Units of 1st rate constant order reaction are sec^{-1} and for zero order reaction, these are $mol\ litre^{-1}\ sec^{-1}$ *i.e.* $M\ sec^{-1}$.

137. (c) This reaction is bimolecular and first order of reaction.

138. (c) $t_{1/2} = \frac{0.693}{k}$ Given $t_{1/2} = 693$ sec

$693 = \frac{0.693}{k}$, $k = \frac{693\times10^{-3}}{693}$;

$k = 10^{-3} = 0.001\ \text{sec}^{-1}$.

139. (d) $2A + B \rightarrow C + B$

Rate = $k[A]^2[B]^1$

$\therefore O.R. = 2+1 = 3$ and molecularity is $3[2A + B]$.

140. (c) In photochemical reactions the rate of reaction is independent of the concentration of reacting species.

141. (c) We know that $k = \frac{2.303}{t}\log\frac{a}{a-x}$

$10^{-3} = \frac{2.303}{t}\log\frac{a}{(a-\frac{2a}{3})}$, $10^{-3} = \frac{2.303}{t}\log$

$10^{-3} = \frac{2.303}{t}\times0.4771$, $t = \frac{2.303\times0.4771}{10^{-3}}$

$= 3300$ sec

142. (c) $R = K(A)^2$, $R' = K(2A)^2$, $\therefore \frac{R'}{R} = 4$

$R = K(A)^2$, $R' = K(3A)^2$, $\frac{R'}{R} = 9$

144. (a) $k = \frac{2.303}{t}\log\left(\frac{a}{a-x}\right)$

$k = \frac{2.303}{32}\log\left(\frac{100}{100-75}\right)$ .... (i)

$k = \frac{2.303}{t}\log\left(\frac{100}{100-50}\right)$ ....(ii)

from the two equation (i) and (ii), $t = 16$ minutes.

146. (c) The relation between half – life period and initial concentration (c) for a nth order reaction is given by $t_{1/2} \propto \frac{1}{C^{n-1}}$ for first order reaction $(n=1)$.

$t_{1/2} \propto \frac{1}{C^{1-1}}$ or $t_{1/2} \propto C^0$.

147. (c) $R = k[NO]^2[O_2]$, $R' = k[2NO]^2[2O_2]$

$R' = k\times4[NO]^2[O_2] = k\times8[NO]^2[O_2]$

$\frac{R'}{R} = \frac{k\times8[NO]^2[O_2]}{k[NO]^2[O_2]} = 8$

148. (b) For zero order reaction $r = k$.

149. (b) $k = \frac{2.303}{t}\log\frac{0.8}{0.6} = 2.303\log\frac{4}{3}$

$t = \frac{2.303}{k}\log\frac{0.9}{0.675} = \frac{2.303}{k}\log\frac{4}{3}$; $t = 1$ *hour*.

150. (a) For zero order reaction

Velocity constant $= \frac{dx}{dt} = \frac{\text{Concentration}}{\text{Time}}$

Unit $= \text{concentration}\times\text{time}^{-1}$.

151. (d) $H_2 + Br_2 \rightleftharpoons 2HBr$ is a 1.5 order reaction

i.e., $K = [H_2][Br_2]^{1/2}$.

152. (a) When in any chemical reaction, one of the reactant is present in large excess, then the second order reaction becomes first order reaction and is known as pseudo unimolecular reaction *e.g.,*

$CH_3COOCH_3 + H_2O \xrightarrow{H^+} CH_3COOH + CH_3OH$

in this reaction molecularity is 2 but order of reaction is found to be first order experimentally, so it is an example of pseudo unimolecular reaction.

153. (d) $K = \frac{0.693}{t_{1/2}} = \frac{0.693}{10\text{years}}$

If initial concentration $a = 10\ gm$ and final concentration $x = \frac{a}{2} = 5\ gm$

then, $t = \frac{2.303}{K}\log\frac{a}{a-x}$

$= \frac{2.303}{.693}\times 10\times \log\frac{10}{5}$

$= \frac{2.303\times 10\times \log 2}{.693}$

$= \frac{2.303\times 10\times 0.301}{0.693} = 10$ years.

154. (c) The concentration of the reactants decrease from 0.8 to 0.4 in 15 *min* i.e., $T_{1/2} = 15\,min$, concentration from 0.1*m* to 0.025 will fall in 2 half lives so total time taken $= 2\times T_{1/2} = 2\times 15 = 30$ *min*.

155. (c) $K = \frac{2.303}{1\,hr}\log\frac{100}{25} = \frac{2.303}{t}\log\frac{100}{50}$

$\therefore\ \log 4 = \frac{1}{t}\log 2$

$\therefore\ 2\log 2 = \frac{1}{t}\log 2;\ t = \frac{1}{2}\,hr.$

156. (b) $x_{(g)} \to y_{(g)} + z_{(g)}$

The reaction is a first order reaction hence,

$K = \frac{0.693}{t_{1/2}} = \frac{2.303}{t}\log\frac{a}{a-x} = \frac{0.693}{10\text{ min}}$

$= \frac{2.303}{t}\log\frac{a}{a/10} = \frac{0.693}{10} = \frac{2.303}{t}\log 10$

$\therefore\ t = \frac{2.303\times 10}{.693} = 33\,\text{min}.$

157. (a) For the first order reaction $t = \frac{2.303}{K}\log\frac{a}{a-x}$

Given: $a = 0.5\ mol/litre$; $a - x = 0.05\ ,mol/litre$

$K = 6\sec^{-1}$.

$t = \frac{2.303}{6}\log\frac{0.5}{0.05} = \frac{2.303}{6}\log 10$

$= \frac{2.303}{6} = 0.384\sec.$

158. (b) The radioactive disintegration reactions are of first order because in this rate of disintegration depends on the concentration term of radioactive material only.

159. (d) Rate $\left(\frac{dx}{dt}\right) = K\,.\,c$; $1.5\times 10^{-2} = K\times 0.5$

For first order

$K = \frac{1.5\times 10^{-2}}{0.5} = 3\times 10^{-2}\ minute^{-1}$

$t_{1/2} = \frac{.693}{K} = \frac{.693}{3\times 10^{-2}} = 23.1\ minute.$

160. (c) For first order reaction $K = \frac{2.303}{t}\log\frac{a}{a-x}$

Given: $a = \frac{1}{10} = .1m$; $a - x = \frac{1}{100} = .01m$; $t =$ 500 *sec*

$\therefore\ K = \frac{2.303}{500}\log\frac{.10}{.01} = \frac{2.303}{500}\log 10$

$= \frac{2.303}{500} = 0.004606 = 4.6\times 10^{-3}\sec^{-1}.$

161. (b) For zero order reaction, rate of reaction is independent of concentration $R = K[\text{Reactant}]^0$

162. (b) The radioactive disintegration reactions are of first order because in this rate of disintegration depends on the concentration term of radioactive material only.

163. (b) $t_{1/2} \propto a^{1-n} \Rightarrow \frac{0.1}{0.4} = \frac{(200)^{1-n}}{(50)^{1-n}} \Rightarrow$

$\frac{1}{4} = \left[\frac{4}{1}\right]^{1-n} = \left[\frac{1}{4}\right]^{n-1}$

$\Rightarrow \frac{1}{4^1} = \frac{1}{4^{n-1}}\ \therefore\ n - 1 = 1;\ n = 2.$

164. (abd) By Vant's Hoff equation, $\frac{d\ln k}{dt} = \frac{\Delta H^o}{RT^2}$

or $\ln k_p = -\frac{\Delta H^o}{RT} + I$. Hence (a) is correct (b) is also correct as plot of log (X) vs time is linear. (c) is wrong because $p \propto T$ at constant volume. (d) is correct by Boyle's law.

165. (ad) (a) is correct because degree of dissociation $= 1 - e^{-kt}$ at any time *t*.

(b) is wrong because plot of log [A] vs *t* is a straight line

(c) is wrong because time taken for 75% reaction is two half life.

(d) is correct because in $k = Ae^{-E_a/RT}$, $E_{a/RT}$ is dimensionless hence *A* has the unit of *K*.

166. (b) $aA \to xP$

Rate of reaction = $[A]^a$

Order of reaction = *a*

$[A]_1 = 2.2\ mM$, $r_1 = 2.4\ m\,M\,s^{-1}$ ...(i)

$[A]_2 = 2.2/2\ mM$, $r_1 = 0.6\ m\,M\,s^{-1}$ or, $\frac{2.4}{4}$ ...(ii)

On reducing the concentration of *A* to half, the rate of reaction is decreased by four times.

Rate of reaction = $[A]^2$

Order of reaction = 2.

167. (d) Order of a reaction can be fractional.

168. (b) $t_{1/4} = \frac{2.303}{K}\log\frac{1}{1-\frac{1}{4}} = \frac{0.29}{K}$.

169. (d) $R = K[A]$

$2\times10^{-5} = K\times10^{-2}$

$K = 2\times10^{-3}\ \text{sec}^{-1}$

$t_{1/2} = \frac{.693}{K} = \frac{.693}{2\times10^{-3}} = \frac{693}{2} = 347\,\text{sec}$

170. (b) $R = k[B]^n$; $\frac{1}{4}R = k[2B]^n$; $4 = \left(\frac{1}{2}\right)^n$; $4 = 2^{-n}$; $n = -2$.

171. (c) $T = t_{1/2}\times n$ *i.e.* $12 = 3\times n \Rightarrow n = 4$

$N = N_0\left(\frac{1}{2}\right)^n \Rightarrow \frac{N}{N_0} = \left(\frac{1}{2}\right)^4 = \frac{1}{16}$

172. (c) $K = 1.7\times10^{-5}s^{-1}$

$t_{1/2} = \frac{0.693}{K} = \frac{0.693}{1.7}\times10^5 = 11.32h$

173. (c) $A + B \rightarrow C$

On doubling the concentration of A rate of reaction increases by four times. Rate $\propto [A]^2$

However on doubling the concentration of B, rate of reaction increases two times. Rate $\propto [B]$

Thus, overall order of reaction = 2 + 1= 3.

174. (a) In case of zero order reaction, the concentration of reactant decreases linearly with time, as its rate is independent of the concentration of the reactants.

Collision theory, Energy of activation and Arrhenius equation

1. (b) The increase in collision frequency brings in an increase in effective collisions and thus rate of reaction increases.

2. (b) All collisions are not effective and does not result in the formation of the products

3. (b) The increase in collision frequency brings in an increase in effective collisions and thus rate of reaction increases.

4. (c) The increase in collision frequency brings in an increase in effective collisions and thus rate of reaction increases.

5. (a) Slower reaction rate indicates higher energy of activation.

6. (d) Energy of activation decreases, rate of reaction will increases.

7. (d) Number of collision depend upon pressure, concentration and temperature.

9. (c) The definition of activation energy.

10. (b) Activation energy is the energy needed by reactant molecules to gain threshold energy level.

11. (d) All other are different forms of Arrhenius equation.

12. (d) Increase in the rate of reaction is determined by the increase in the number of effective collisions.

13. (a) Energy of activation reduced by increasing temperature.

14. (d) The definition of threshold energy.

15. (a) The definition of activation energy.

16. (b) When the temperature is increased, heat energy is supplied which increases the kinetic energy of the reacting molecules. this will increase the number of collisions and ultimately the rate of reaction will be enhanced.

17. (d) In exothermic and endothermic reactions will be more and less than E_a respectively.

19. (b) The value of activation energy for a chemical reaction primarily dependent on the nature of reacting species.

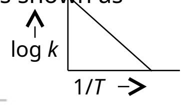
20. (a) Arrhenius equation is $\log k = \log A - \frac{E_a}{RT}$

22. (a) A graph plotted between $\log k$ vs $\frac{1}{T}$ for calculating activation energy.

24. (b) When $E_a = 0$ rate constant is independent of temperature.

25. (a) It is modified form of Arrhenius equation.

28. (b) A graph plotted between $\log k$ Vs $\frac{1}{T}$ for calculating activation energy is shown as from Arrhenius equation



$\log k = \log A - \frac{E_A}{2.303\ RT}$

30. (c) It is Arrhenius equation.

31. (b) $\log\frac{K_2}{K_1} = \frac{E_a}{2.303R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right]$

If $\frac{K_2}{K_1} = 2$

$\log 2 = \frac{E_a}{2.303\times8.314}\left[\frac{1}{300} - \frac{1}{310}\right]$

$E_a = .3010\times2.303\times8.314\left(\frac{300\times310}{10}\right)$

$= 53598.59\ Jmol^{-1} = 54\ kJ$.

32. (d) When $E_a = 0$, the rate of reaction becomes independent of temperature.

(E_a = Energy of activation).

33. (c) When *k* increases, rate of reaction also increases, $k = \frac{pz}{e^{E/RT}}$ for k to increase *p*, *z*, *T* should increase and *E* should decrease. ($e \approx 2.7$).

34. (c) Endothermic reactions are those which involve absorption of heat. High activation energy means potential energy of product must be much greater than reactants.

35. (a) For endothermic reaction Δ*H* = *+ve*

Then from equation $\Delta H = E_{a_{F.R.}} - E_{a_{B.R.}}; E_{B.R.} < E_{F.R.}$

36. (a) Arrhenius suggested an equation which describes rate constant (*K*) as a function of temperature.

$$K = Ae^{-E_a/RT}$$

$$\ln K = \ln A - e^{E_a/RT}$$

Photochemical reactions

2. (a) $H_2O \xrightarrow{\text{Photolysis}} OH^- + H^+$

3. (c) Stark - Einstein was given the law of photochemical equivalence.

4. (b) In photochemical reaction the rate of formation of product is directly proportional to the intensity of absorbed light.

Critical Thinking Questions

1. (a) For the given reaction :

$$-\frac{\Delta[I_2]}{\Delta t} = -\frac{\Delta[H_2]}{\Delta t} = \frac{1}{2}\frac{\Delta[HI]}{\Delta t}$$

2. (c) $-\frac{1}{3}\frac{d[A]}{dt} = \frac{1}{2}\frac{d[B]}{dt} \quad \therefore \frac{d[B]}{dt} = -\frac{2}{3}\frac{d[A]}{dt}$

3. (a) Concentration of reactants decreases while concentration of product increases.

4. (d) $R = K(A)^n(B)^m$

$$R' = K(2A)^n\left(\frac{B}{2}\right)^m = K(A)^n 2^n (B)^m 2^{-m}$$

$$= K(A)^n(B)^m 2^{n-m},$$

$$\frac{R'}{R} = \frac{K(A)^n(B)^m 2^{n-m}}{K(A)^n(B)^m} = 2^{n-m}$$

5. (c) $\ln K = \ln \quad -\frac{E_a}{RT}$ is Arrhenius equation. Thus plots of ln *K* vs 1/T will give slope $= -E_a/RT$ or $-E_a/2.303R$.

6. (c) For a reaction E_a for forward reaction $= E_a$ for backward reaction + ΔH.

7. (c) As

$$K^{\cdot} > K^{\cdot\cdot}, E_a^{\cdot} < E_a^{\cdot\cdot}$$

(Greater the rate constant, less is the activation energy).

8. (b) $T_2 = T(say), T = 25^oC = 298K,$

$$E_a = 104.4 \text{ kJ } mol^{-1} = 104.4 \times 10^3 \text{ J } mol^{-1}$$

$$K_1 = 3 \times 10^{-4}, K_2 = ?,$$

$$\log\frac{K_2}{K_1} = \frac{E_a}{2.303R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right]$$

$$\log\frac{K_2}{3 \times 10^{-4}} = \frac{104.4 \times 10^3 \text{J } mol^{-1}}{2.303 \times (8.314 \text{ J } k^{-1} mol^{-1})}$$

$$\left[\frac{1}{298K} - \frac{1}{T}\right] \text{As T} \to \infty, \frac{1}{\text{T}} \to 0$$

$$\therefore \log\frac{K_2}{3 \times 10^{-4}} = \frac{104.4 \times 10^3 \text{ J } mol^{-1}}{2.303 \times 8.314 \times 298}$$

$$\log\frac{K_2}{3 \times 10^{-4}} = 18.297, \frac{K_2}{3 \times 10^{-4}}$$

$= 1.98 \times 10^{18}$ or

$$K_2 = (1.98 \times 10^{18}) \times (3 \times 10^{-4}) = 6 \times 10^{14} s^{-1}$$

9. (a) Because reaction is exothermic

10. (d) $k = Ae^{-E^0/RT}$ $\quad \underset{y}{\log K} = \underset{c}{\log A} - \underset{mx}{E^o}/RT$

$\therefore \log K \quad Vs \quad \frac{1}{T}$.

11. (c) $\log\frac{K_2}{K_1} = \frac{E_a}{2.303R}\left[\frac{T_2 - T_1}{T_1T_2}\right]$

12. (a) $2.303\log\frac{K_2}{K_1} = \frac{E_a}{R}\left[\frac{T_2 - T_1}{T_1T_2}\right]$

$$\log\frac{K_2}{K_1} = \frac{9.0 \times 10^3}{2.303 \times 2}\left[\frac{308 - 298}{308 \times 298}\right]$$

$$\frac{K_2}{K_1} = 1.63;\ K_2 = 1.63K_1; \frac{1.63K_1 - K_1}{K_1} \times 100 = 63.0$$

13. (d) Combustion is an exothermic process, which is expected to be favoured by low temperature, but it is not true. Combustion include burning of particles which takes place at higher temperature. Thus at high temperature due to combustion of more particles, the reaction proceeds at higher rate.

14. (d) Rate constant $= 2.3 \times 10^{-2}\ \sec^{-1}$

It means it is a first order reaction (because unit of rate constant is $\sec^{-1}$)

For first order reaction $K = \frac{1}{t}\ln\frac{a}{a-x}$

$$Kt = \ln\frac{a}{a-x} = \ln\frac{[N_2O_5]_0}{[N_2O_5]_t}$$

15. (b) Because as reaction progresses the amount of acetic acid increases.

16. (d) Half life of a reaction is found to be inversely proportional to the cube of initial concentration. The order of reaction is 4.

17. (a) It is similar to $y = mx + c$

18. (b) $r = K[A]^n$, $100r = K[10A]^n$

Thus $\frac{1}{100} = \left(\frac{1}{10}\right)^n$ or $n = 2$

19. (c) Concentration will fall from 0.1 M concentration to 0.025 M concentration within 2 half lives.

$2 \times T_{1/2} = 40\ min$

$\therefore\ T_{1/2} = 20\ min$

Rate of reaction = K . c $= \frac{0.693}{T_{1/2}}.c$

$$= \frac{0.693}{20} \times 10^{-2} M/\text{min}$$

$$= 3.47 \times 10^{-4} M/\text{min}^{-1}.$$

20. (e) % distribution of $B = \frac{K_1}{K_1 + K_2} \times 100$

$$= \frac{1.26 \times 10^{-4}}{1.26 \times 10^{-4} + 3.8 \times 10^{-4}} \times 100$$

$B\% = 76.83\%$

$$\%\text{Distribution of } C = \frac{K_2}{K_1 + K_2} \times 100$$

$$= \frac{3.8 \times 10^{-4}}{1.26 \times 10^{-4} + 3.8 \times 10^{-4}} \times 100$$

$C\% = 23.17\%$

Assertion and Reason

1. (b) Instantaneous rate of a reaction is equal to small change in concentration (dx) during a small interval of time (dt) at that particular instent of time divided by the time interval.

2. (b) Molecularity of a reaction can be defined only for an elementary reaction because complex reaction does not take place in one single step and it is almost impossible for all the total molecules of the reactants to be in a state of encounter simultaneously.

3. (b) For a zero order reaction, $t_{1/2} = [A_0]/2K$.

4. (b) According to Arrhenius equation, $K = Ae^{-E_a/RT}$ when $E_a = 0, K = A$.

6. (a) For a first order reaction, $K = \frac{2.303}{t}\log\frac{a}{a-x}$, where a is initial concentration, and x is the amount reacted in time t. For half-life $x = a/2$, $t = t_{1/2}$

$$K = \frac{2.303}{K}\log\frac{a}{a - a/2}$$

$$t_{1/2} = \frac{2.303}{K}\log 2 = \frac{0.693}{K}.$$

7. (d) $H_2 + Cl_2 \rightarrow 2HCl$ has much higher quantum efficiency than $H_2 + Br_2 \rightarrow 2HBr$. The first step of secondary process of $H_2 + Cl_2 \rightarrow 2HCl$ is exothermic while the same for $H_2 + Br_2 \rightarrow 2HBr$ is endothermic.

8. (e) Vision is a fast photochemical reaction in which the compound, retinal, present in the eye undergoes isomerisation by absorbing a photon of light.

9. (a) The emission of cold light during a chemical reaction is called chemiluminescence.

10. (d) The rate reaction is never negative. Minus sign used in expressing the rate only shows that the concentration of the reactant is decreasing.

11. (a) Rate expression $\frac{dx}{dt} = K[A]^m[B]^n$

Shows that the total order of reactions is $m + n + 0 = m + n$ as the rate of reaction is independent of concentration of C, *i.e.* the order with respect to C is zero. This is the reason that C does not figure in the rate expression.

Chemical Kinetics

1. A catalyst
   (a) Increases the average kinetic energy of reacting molecules
   (b) Increases the activation energy
   (c) Alters the reaction mechanism
   (d) Increases the frequency of collisions of reacting species

2. The rate law for the reaction $\mathrm{RCl} + \mathrm{NaOH}(aq) \rightarrow \mathrm{ROH} + \mathrm{NaCl}$ is given by, Rate = k [RCl]. The rate of the reaction will be
   (a) Doubled on doubling the concentration of sodium hydroxide
   (b) Halved on reducing the concentration of alkyl halide to one half
   (c) Decreased on increasing the temperature of the reaction
   (d) Unaffected by increasing the temperature of the reaction

3. A reaction involving two different reactants
   (a) can never be a first order reaction
   (b) can never be a second order reaction
   (c) can never be a unimolecular reaction
   (d) can never be a bimolecular reaction

4. The rate constant of a reaction increases with increase of temperature because
   (a) The activation energy increases
   (b) The population of activated molecules increases.
   (c) The activation energy decreases
   (d) The population of activated molecules decreases.

5. The rate constant (k') of one of the reaction is found to be double that of the rate constant (k'') of another reaction. Then the relationship between the corresponding activation energies of the two reactions (E_a' and E_a'') can be represented as
   (a) $E_a' > E_a''$ (b) $E_a' < E_a''$ (c) $E_a' = E_a''$ (d) $E_a' = 4E_a''$

6. What will be the order of the reaction if doubling the concentration of a reactant increases the rate by a factor of 4 and trebling the concentration of the reactant by a factor of 9?
   (a) First order (b) Zero order (c) Second order (d) Third order

7. For an endothermic reaction, where ΔH represents the enthalpy of the reaction in kJ/mol, the minimum value for the energy of activation will be
   (a) less than ΔH (b) zero (c) more than ΔH (d) equal to ΔH

8. Select the law that corresponds to data shown for the following reaction
   $A + B \rightarrow \text{Products}$

Exp.	[A]	[B]	initial rate
1	0.012	0.035	0.1
2	0.024	0.070	0.8
3	0.024	0.035	0.1

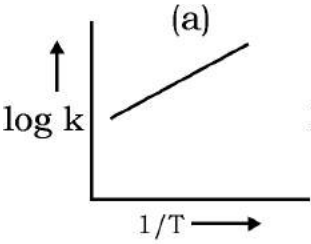
4	0.012	0.070	0.8

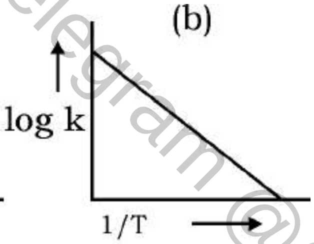
(a) rate = $k\,[B]^3$ (b) rate = $k\,[B]^4$
(c) rate = $k\,[A]\,[B]^3$ (d) rate = $k\,[A]^2\,[B]^2$

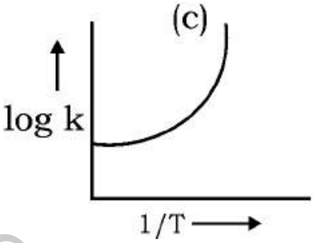
9. According to the Arrhenius equation a straight line is to be obtained by plotting the logarithm of the rate constant of a chemical reaction (log k) against
(a) T (b) log T (c) 1/T (d) log 1/T.

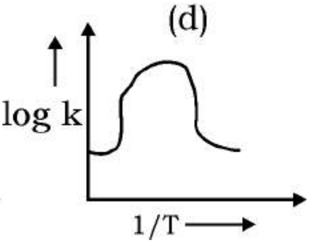
10. For a first order reaction, the plot of log k against 1/T is a straight line. The slope of the line is equal to
(a) $-\frac{E_a}{R}$ (b) $-\frac{2.303}{E_a R}$ (c) $-\frac{E_a}{2.303}$ (d) $-\frac{E_a}{2.303\ R}$

11. A graph plotted between log k vs 1/T for calculating activation energy is shown by









12. For the reaction system $2NO(g) + O_2(g) \rightarrow 2NO_2(g)$ the volume is suddenly reduced to half its value by increasing the pressure on it. If the reaction is of first order with respect to O_2 and second order with respect to NO, the rate of reaction will be
(a) diminish to one-eight of its initial value
(b) increase to eight times of its initial value
(c) increase to four times its initial value
(d) diminish to one-fourth of its initial value

13. The rate of a gaseous reaction is equal to k [A][B]. The volume of the reaction vessel containing these gases is suddenly reduced to one-fourth of the initial volume. The rate of the reaction would be
(a) 1/16 (b) 16/1 (c) 1/8 (d) 8/1.

14. The rate law for a reaction between the substances A and B is given by Rate = $k[A]^n[B]^n$. On doubling the concentration of A and halving the concentration of B, the ratio of the new rate to the earlier rate of the reaction will be as
(a) $m + n$ (b) $(n - m)$ (c) $2^{(n-m)}$ (d) $\frac{1}{2^{(m+n)}}$

15. For the reaction, 2A + B → Products, the following initial rates were obtained at various initial concentrations:

[A]	[B]	Rate (mol l^{-1}sec^{-1})

0.1M	0.2M	0.46
0.2M	0.2M	1.84
0.2M	0.1M	0.92

The rate law for the reaction is

(a) Rate = $k[A]^2[B]^0$ (b) Rate = $k[A][B]$

(c) Rate = $k[A]^2[B]$ (d) Rate = $k[A][B]^2$

16. If initial concentration is reduced to 1/4th in a zero order reaction, the time taken for half the reaction to complete
(a) remains same (b) becomes 4 times
(b) becomes one-fourth (d) doubles

17. In the first order reaction, 75% of the reactant disappeared in 1.386 *h*. Calculate the rate constant of reaction.
(a) $3.6 \times 10^{-3} s^{-1}$ (b) $2.8 \times 10^{-4} s^{-1}$ (c) $17.2 \times 10^{-3} s^{-1}$ (d) $1.8 \times 10^{-3} s^{-1}$

18. An endothermic reaction A → B has an activation energy of 15 kcal/mole and the energy of reaction is 5 kcal/mole. The activation energy for the reaction B → A is
(a) 20 kcal/mole (b) 15 kcal/mole (c) 10 kcal/mole (d) zero

19. The rate of a chemical reaction doubles for every 10^0C rise in temperature. If the temperature is increased by 60^0C, the rate of reaction increases by about
(a) 20 times (b) 32 times (c) 64 times (d) 128 times

20. The rate constant of a reaction at temperature 200 K is 10 times less than the rate constant at 400 K. What is the activation energy (E_a) of the reaction?
(a) 1842.4 R (b) 921.2 R (c) 460.6 R (d) 230.3 R

21. If *a* is the initial concentration and *k* is the rate constant of a zero order reaction, the time for the reaction to go to completion will be
(a) *k/a* (b) *a/k* (c) *a/2k* (d) *k/2a*

22. The rate constant of *n*th order has units
(a) $litre^{1-n} mol^{1-n} sec^{-1}$ (b) $Mole^{1-n} litre^{1-n} sec$
(c) $Mol^{1-n^2} litre^{n^2} sec^{-1}$ (d) $Mole^{1-n} litre^{n-1} sec^{-1}$

23. For the decomposition of N_2O_5 at a particular temperature, according to the equations $2N_2O_5 \rightarrow 4NO_2 + O_2$, $N_2O_5 \rightarrow 2NO_2 + \frac{1}{2}O_2$
the activation energies are E_1 and E_2 respectively. Then
(a) $E_1 > E_2$ (b) $E_1 < E_2$ (c) $E_1 = 2E_2$ (d) $E_1 = E_2$

24. The hydrolysis of ethyl acetate was carried out separately with 0.05 M HCl and 0.05 M H_2SO_4. The rate constants were found to be k_1 and k_2 respectively. Then
(a) $k_1 = k_2$ (b) $k_1 > k_2$ (c) $k_1 < k_2$ (d) $k_2 = 2k_1$

25. A certain reaction A + B → P is of first order with respect to each reactant. If $[A]_0$ =0.1 M, $[B]_0$ = 5.0 M and the second order rate constant k is $6 \times 10^{-3} M^{-1} s^{-1}$, the half-life of the reaction in seconds is
(a) 23.5 (b) 27.7 (c) 33.3 (d) 115.5

26. Consider the following statements:
The rate law for the acid catalysed hydrolysis of an ester being given as Rate = k $[H^+]$ [ester] = k' [ester]. If the acid concentration is doubled at constant ester concentration
1. the second order rate constant, k is doubled
2. the pseudo first order rate constant, k is doubled
3. the rate of the reaction is doubled.

Which of the above statements are correct?
(a) 1 and 2 (b) 2 and 3 (c) 1 and 3 (d) 1, 2 and 3

Chemical Kinetics

ANSWER KEY

Q.No.	Ans.	Q.No.	Ans.	Q.No.	Ans.
1.	C	11.	B	21.	B
2.	B	12.	B	22.	D
3.	C	13.	B	23.	D
4.	B	14.	C	24.	C
5.	B	15.	C	25.	A
6.	C	16.	C	26.	B
7.	C	17.	B		
8.	A	18.	C		
9.	C	19.	C		
10.	D	20.	B		

Solution

1. A catalyst alters the reaction mechanism.

2. As rate = k [RCl], on decreasing the concentration of RCl to half, the rate will also be halved.

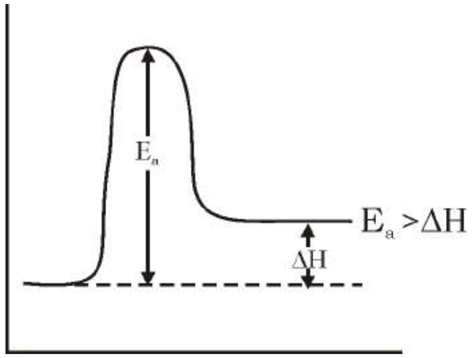
3. A reaction with two reactants cannot be unimolecular.

4. With increase in temperature, population of activated molecules increases.

5. As $k' > k'', E_a' < E_a''$ (Greater the rate constant, less is the activation energy).

6. $2^2 = 4,\ 3^2 = 9$

7.



8. From 1 and 3, keeping [B] const, [A] is doubled, rate remains unaffected. Hence rate is independent of [A]. From 1 and 4, keeping [A] constant, [B] is doubled, rate becomes 8 times. Hence rate $\propto [B]^3$.

9. A straight line is obtained when log *k* is plotted against 1/T.

10. $\log\ k = -\frac{E_a}{2.303RT} + \log A.$

Hence slope will be = $-\frac{E_a}{2.303R^{+}}$.

11. (b) according to Arrhenius equation.

12. Rate = $k[NO]^2[O_2]$. Initially rate = ka^2b. If volume is reduced to half, concentration are doubled so that new rate

$$= k(2a)^2(2b) = 8ka^2b \text{ i.e. } 8 \text{ times.}$$

13. Initially, rate = $K[A][B] = kab$
When volume of the vessel is reduced to one-fourth, concentrations become 4 times. Hence new rate = k (4*a*) (4*b*) = 16 *kab* i.e. it becomes 16 times.

14. Earlier rate = ka^nb^m

New rate = $k(2a)^n\left(\frac{b}{2}\right)^m$

$$\frac{\text{New rate}}{\text{Earliar rate}} = \frac{2^na^nb^ma^{-m}}{a^nb^m} = 2^n.2^{-m} = 2^{n-m}$$

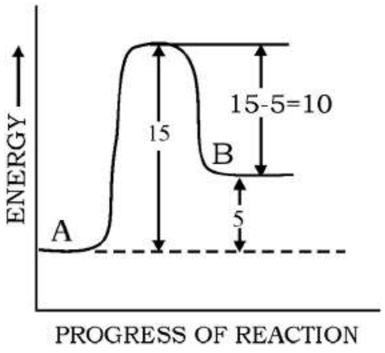
15. $\text{Rate} = k[A]^2[B]$

16. For zero order reactions, $t_{1/2} = \frac{[A_0]}{2k}$

When $[A_0]$ is reduced to $\frac{1}{4}$th, $t_{1/2}$ will become $\frac{1}{4}$th.

17. $k = \frac{2.303}{1.386 \times 60 \times 60}\log\frac{a}{a-0.75a} = \frac{2.303}{1.386 \times 60 \times 60}\log 4 = 2.8 \times 10^{-4}\,s^{-1}$

18.



19. 10^0 increase has been made 6 times, the rate will increase 2^6 = 64 times.

20. At $T_1 = 200\text{K} \text{ if } k_1 = k$, then at

$$T_2 = 400\text{ K},\ k_2 = 10\text{ k}$$

$$\therefore \log\frac{10\text{k}}{\text{k}} = \frac{E_a}{2.303R}\left(\frac{400-200}{400\times200}\right) \quad \text{or} \quad E_a = 921.2R$$

21. For zero order, $\frac{dx}{dt} = k$ or $dx = kdt$ Or $x = kt + \text{I}$. When t = 0, x = 0. So, I = 0.

Hence $x = kt$ or $t = \frac{x}{k}$.

For completion, $x = a$. Hence $t = \frac{a}{k}$.

22. $$\frac{dx}{dt} = k(\text{Conc.})^n \text{ or } k = \frac{\text{Conc.}}{\text{Time}}\times\frac{1}{(\text{Conc.})^n}$$

$$= (\text{Conc.})^{1-n}\ \text{time}^{-1} = (\text{mol L}^{-1})^{1-n}\ \text{sec}^{-1} = \text{mol}^{1-n}\text{L}^{n-1}\ \text{sec}^{-1}$$

23. Activation energy of a particular reaction is constant at constant temperature.

24. In presence of acid, hydrolysis of ethyl acetate is a pseudo-unimolecular reaction but the actual value of *k* depends upon the concentration of H^+ ion. As H_2SO_4 is stronger acid than HCl and moreover H^+ ions produced from 0.05 M H_2SO_4 is double than those produced from 0.05 M HCl, therefore $k_2 >> k_1$ or $k_1 < k_2$.

25. For 2nd order reactions, $k = \frac{2.303}{t\{[A_0]-[B]_0\}}\log\frac{[B]_0[A]}{[A]_0[B]}$

When $t = t_{1/2}, [A] = [A]_0/2, = 0.1/2 = 0.05$

At that time [B] = 5-0.05 = 4.95 M

$$\therefore t_{1/2} = \frac{2.303}{6\times10^{-3}(0.1-5.0)}\log\frac{5\times0.05}{0.1\times4.95} \approx \frac{2.303}{6\times10^{-3}(-4.9)}\log\frac{1}{2} \approx 23.5\text{s}$$

26. Pseudo first order rate constant is doubled as well as rate of reaction is doubled. It may be noted that in presence of acid, hydrolysis of ethyl acetate is a pseudo-unimolecular reaction but the actual value of k depends upon the concentration of H^+ ions, otherwise rate constant of a reaction is constant at constant temperature.

Chemical Kinetics

SET Self Evaluation Test - 11

1. The temperature coefficient of most of the reactions lies between **[MP PET 1999]**

(a) 1 and 3 (b) 2 and 3

(c) 1 and 4 (d) 2 and 4

2. The influence of temperature on the rate of reaction can be found out by **[AFMC 2001]**

(a) Clapeyron–Claussius equation

(b) Gibbs–Helmholtz equation

(c) Arrhenius equation

(d) Vander Waal's equation

3. The mechanism for the reaction is given below

$2P + Q \rightarrow S + T$

$P + Q \rightarrow R + S$ (slow)

$P + R \rightarrow T$ (fast)

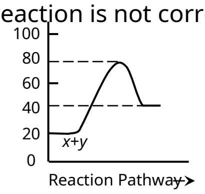
The rate law expression for the reaction is

[Kurukshetra CEE 2002]

(a) $r = k[P]^2[Q]$ (b) $r = k[P][Q]$

(c) $r = k[A][R]$ (d) $r = k[P]^2$

4. Consider the following energy profile for the reaction. $X + Y = R + S$. Which of the following deductions about the reaction is not correct



(a) The energy of activation for the backward reaction is 80 *kJ*

(b) The forward reaction is endothermic

(c) ΔH for the forward reaction is 20 *kJ*

(d) The energy of activation for the forward reaction is 60 *kJ*

5. The minimum energy required for molecules to enter into the reaction is called

[KCET 1986; EAMCET 1992; MP PMT 1993; MP PET 1994]

(a) Potential energy

(b) Kinetic energy

(c) Nuclear energy

(d) Activation energy

6. The minimum energy necessary to permit a reaction is

[NCERT 1989]

(a) Internal energy

(b) Threshold energy

(c) Activation energy

(d) Free energy

7. The formation of gas at the surface of tungsten due to adsorption is the reaction of order **[AIEEE 2002]**

(a) 0

(b) 1

(c) 2

(d) insufficient data

8. The time of completion of 90% of a first order reaction is approximately **[MP PET 2002]**

(a) 1.1 times that of half life

(b) 2.2 times that of half life

(c) 3.3 times that of half life

(d) 4.4 times that of half life

9. In a photochemical reaction, the ratio of number of dissociate molecules and number of quanta of absorbed energy is called

(a) Einstein

(b) Quantum efficiency

(c) Quantum constant

(d) Planck constant

10. A reaction rate constant is given by

$k = 1.2 \times 10^{14} e^{-(25000/RT)} \sec^{-1}$

It means **[MP PET 1995]**

(a) $\log k$ versus $\log T$ will give a straight line with slope as – 25000

(b) $\log k$ versus T will give a straight line with slope as – 25000

(c) $\log k$ versus $\log 1/T$ will give a straight line with slope as – 25000

(d) $\log k$ versus $1/T$ will give a straight line

Answers and Solutions

(SET -11)

1. (b) Temperature coefficient = $\frac{K_{35^\circ C}}{K_{25^\circ C}}$ = between 2 and 3.

2. (c) Arrihenius equation is : $K = Ae^{-E_a/RT}$

3. (b) The rate law expression for the reaction is $r = k[P][Q]$.

4. (a) E_a of backward reaction $= 80 - 40 = 40kJ$

Hence (a) statement is wrong.

5. (d) The energy necessary for molecules to undergoes chemical reaction is known as Activation energy.

6. (b) Molecules undergoing reaction should cross over the minimum energy barrier or energy level known as threshold energy.

7. (a) The order of reaction for the formation of gas at the surface of tungsten due to adsorption is zero .

8. (c) For a first order reaction

$$K = \frac{2.303}{t}\log\frac{a}{(a-x)}$$

$$t = \frac{2.303}{k}\log\frac{100}{(100-90)}$$

$$= \frac{2.303 \times t_{1/2}}{0.593} \times \log\frac{100}{10}$$

$$= 3.3 \times t_{1/2} \times \log 10 = 3.3\ t_{1/2}$$

9. (b) It is also known as Quantum yield and indicated by ϕ.

10. (d) According to the Arrihenius equation a straight line is to be `obtained by plotting the logarithm of the rate constant of a chemical reaction (log *K*) against 1/*T*.

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Thermodynamics

Level - 1
Thermodynamics

1. In the reaction $C(s) + O_2(g) \rightarrow CO_2(g) + 93.4$ kcal
   (a) Enthalpy of products is greater than that of reactants
   (b) Enthalpy of products is less than that of reactants
   (c) Enthalpy of products is same as that of reactants
   (d) Enthalpy of products is half of that of reactants.

2. The correct relationship between ΔH and ΔE for an ideal gas at constant temperature is
   (a) $\Delta H = \Delta E - P\Delta V$ (b) $\Delta H = \Delta E + P\Delta V$
   (c) $\Delta H = \Delta E + \Delta P.\Delta V$ (d) $\Delta H = E + P\Delta V$.

3. The enthalpy of reaction at constant volume (ΔE) is related to the enthalpy of reaction at constant pressure (ΔH) as
   (a) $\Delta H = \Delta E - \Delta n_g RT$ (b) $\Delta H = \Delta E + \Delta n_g RT$
   (c) $-\Delta H = -\Delta E + \Delta n_g RT$ (d) None of these is correct.

4. The heat formation of H_2O (l) is— 68.0 kcal, the heat of formation Of H_2O (g) is likely to be
   (a) – 68.0 kcal (b) – 69.4 kcal (c) 80.0 kcal (d) – 58.3 kcal

5. The heats of neutralisation of four acids a, b, c and d when neutralised against a common base are 13.7, 9.4, 11.2 and 12.4 kcal respectively. The weakest among these acids is
   (a) a (b) b (c) c (d) d.

6. For a reversible isothermal process in equilibrium, the entropy change is given by the expression
   (a) $\Delta S = \frac{T}{q_{rev}}$ (b) $\Delta S = \frac{q_{rev}}{T}$ (c) $\Delta S = \frac{\Delta V}{T}$ (d) $\Delta S = \frac{\Delta E}{T}$

7. In a reversible process, $\Delta S_{sys} + \Delta S_{surr}$ is
   (a) > 0 (b) < 0 (c) ≥ 0 (d) $= 0$

8. Which one is true ?
   (a) 1 calorie > 1 erg > 1 Joule (b) 1 erg > 1 calorie > 1 Joule
   (c) 1 calorie > 1 Joule > 1 erg (d) 1 Joule > 1 calorie > 1 erg

9. The entropy of a perfectly crystalline solid at absolute zero is
   (a) positive (b) negative (c) zero (d) not definite

10. When water is added to conc. H_2SO_4 it gets very hot. This happens because dilution of conc. H_2SO_4 is
    (a) an exothermic reaction (b) an endothermic reaction

(c) photochemical reaction (d) hydrolytic reaction.

11. Heat of neutralization of NH_4OH and HCl is
(a) 13.7 kcal/mole (b) <13.7 kcal/mole
(c) >13.7 kcal/mole (d) zero.

12. A solution of 500 ml. of 0.2 M KOH and 500 ml of 0.2 M HCl is mixed and stirred; the rise in temperature is T_1. The experiment is repeated using 250 ml each of solution, the temperature rise is T_2. Which of the following is true?
(a) $T_1 = T_2$ (b) $T_1 = 2T_2$ (c) $T_1 = 4T_2$ (d) $T_2 = 9T_1$

13. Equal volumes of molar hydrochloric acid and sulphuric acid are neutralized by dil. NaOH solution and x kcal and y kcal of heat are liberated respectively. Which of the following is true ?
(a) $x = y$ (b) $x = \frac{1}{2}y$ (c) $x = 2y$ (d)None of these.

14. Heat of neutralisation of strong acid against strong base is constant and is equal to
(a) 13.7 kcal (b) 57 kJ (c) 5.7×10^4 J (d) All of the above.

15. The heat of formation of the compound in the following reaction is
$H_2g + Cl_2(g) \rightarrow 2HCl(g) + 44\ \text{kcal}$
(a)- 44 kcal mol^{-1} (b)-22 kcal mol^{-1}
(c)11 kcal mol^{-1} (d)-88 kcal mol^{-1}

16. The standard Gibb's free energy change, ΔG^o is related to equilibrium constant, K_p as
(a) $K_p = -RT\ \text{In}\ \Delta G^0$ (b) $K_p = \left[\frac{e}{RT}\right]^{\Delta G^0}$
(c) $K_p = -\frac{\Delta G}{RT}$ (d) $K_p = e^{-\Delta G^0/RT}$.

17. Given that $C + O_2 \rightarrow CO_2 \Delta H^0 = -xkj$
$2CO + O_2 \rightarrow 2CO_2 \Delta H^o = -ykj$
the enthalpy of formation of carbon monoxide will be
(a) $\frac{2x - y}{2}$ (b) $\frac{y - 2x}{2}$ (c) $2x - y$ (d) $y = 2x$

18. The energy change of reaction $C_2H_6(g) \rightarrow 2C(g) + 6H(g)$ is X kJ
The bond energy of C – H bond is
(a) X/6kJ (b) X/3 kJ (c) X kJ (d) Indeterminate

19. $S + \frac{3}{2}O_2 \rightarrow SO_3 + 2x\ \text{kcal}$, $SO_2 + \frac{1}{2}O_2 \rightarrow SO_3 + y\ \text{kcal}$

Find out the heat of formation of SO_2

(a) $(y - 2x)$ (b) $(2x + y)$ (c) $(x + y)$ (d) $2x / y$

20. For the reaction $C_3H_8(g) + 5O_2(g) \rightarrow 3CO_2(g) + 4H_2O(l)$ at constant temperature, $\Delta H - \Delta E$ is

(a) + RT (b) – 3 RT (c) + 3 RT (d) – RT

21. The internal energy change when a system goes from state A to B is 40 kJ/ mole. If the system goes from A to B by a reversible path and returns to state A by an irreversible path, what would be the net change in internal energy?

(a) > 40 k J (b) < 40 kJ (c) zero (d) 40 kJ

22. Under the same conditions how many ml of 1 M KOH and 0.5 H_2SO_4 solutions, respectively, when mixed to form a total volume of 100 ml. produce the highest rise in temperature.

(a) 67, 33 (b) 33,67 (c) 40,60 (d) 50,50

23. Enthalpy of neutralisation of HCl with NaOH is x. The heat evolved when 500 ml of 2 NHCl are mixed with 250 ml of 4 N NaOH will be

(a) 500 x (b) 100x (c) x (d) 10 x

24. Based on the following thermochemical equations

$H_2O(g) + C(s) \rightarrow CO(g) + H_2(g); \Delta H = 131\,kJ$

$CO(g) + \frac{1}{2}O_2(g) \rightarrow CO_2(g); \Delta H = -282\,kJ$

$H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(g); \Delta H = -242\,kJ$

$C(s) + O_2(g) \rightarrow CO_2(g); \Delta H = X\ kJ$ the value of X will be

(a) -393 kJ (b) -655 kJ (c) +393 kJ (d) +655 kJ

25. The standard heat of formation in kcal/mole of NO_2 (g) and N_2O_4(g) are 8.0 and 2.0 respectively. The heat of dimerisation of NO_2 i.e. for 2 NO_2 (g) N_2O_4 (g) in kcal is

(a) 10.0 (b) – 6.0 (c) – 12.0 (d) – 14.0

26. Considering the following reactions, $C + \frac{1}{2}O_2 \rightarrow CO\ \Delta H = -26.4\,K.$

$H_2 + \frac{1}{2}O_2 \rightarrow H_2O(l)\ \Delta H = -57.8\,kcal$, ΔH for the reaction
$\mathrm{H_2O + C \rightarrow H_2 + CO}$ is
(a) 62.8 kcal (b) 31.4 kcal (c) —31.4 kcal (d) —84.2 kcal

27. The bond energy of an O-H bond is 109 kcal mol^{-1}. When a mole of water is formed
(a) 218 kcal is released (b) 109 kcal is released
(c) 218 kcal is absorbed (d) 109 kcal is absorbed

28. One mole of an ideal gas at 300 K is expanded isothermally from an initial volume of 1 litre to 10 litres. The ΔE for this process is
(R = 2 cal mol^{-1} K^{-1})
(a) 163.7 cal (b) zero (c) 1381.1 cal (d) 9 lit atom

29. 2 mole of an ideal gas at 27^0 C temperatures is expanded reversibly from 2 lit. to 20 lit. Find entropy change (R = 2 cal/ mol K)
(a) 92.1 (b) 0 (c) 4 (d) 9.2

30. One mole of a non-ideal gas undergoes a change of state (2.0 atm, 3.0L, 95 K) → (4.0 atm, 5.0 L, 245 K) with a change in internal energy, ΔU = 30.0L atm. The change in enthalpy (ΔH) of the process in L atm is
(a) 40.0 (b) 42.3 (c) 44.0
(d) not defined, because pressure is not constant

31. The standard state Gibbs free energy change for the isomerization reaction
$\mathrm{cis-2-pentene}$ □ $\mathrm{trans-2-pentene}$ is -3.67 kJ/mol at 400 K. If more trans-2-pentene is added to the reaction vessel, then
(a) additional trans -2- pentene is formed
(b) more cis – 2– pentene is formed
(c) equilibrium is shifted in the forward direction.
(d) equilibrium remains unaffected.

32. Heat of neutralisation of NaOH and HCl is – 57.3 kJ mol^{-1}. The heat of ionization of water will be
(a) -57.3 kJ mol^{-1} (b) -114.6 kJ mol^{-1}
(c) +57.3 kJ mol^{-1} (d) +114.6 kJ mol^{-1}

33. $\mathrm{HA + OH^- \rightarrow H_2O + A^- + q_1\,kJ}$, $\mathrm{H^+ + OH^- \rightarrow H_2O + q_2\ kJ}$
The enthalpy of dissociation of HA is
(a) $(q_1 + q_2)$ (b) $(q_1 - q_2)$ (c) $(q_2 - q_1)$ (d) $-(q_1 + q_2)$

34. Calculate the work done when 1 mole water at 373 K vaporizes against an atmosphereic pressure of 1.0 atomsphere. Assume ideal gas behaviour

(a) - 6200 J (b) - 306 J (c) - 3100 J (d) - 1550 J

35. Match list I with List II and select the correct answer using the codes given below the lists:

List I	(A) $\left(\frac{\partial G}{\partial p}\right)_T$	(B) $\left(\frac{\partial G}{\partial T}\right)_p$	(C) $\left(\frac{\partial H}{\partial S}\right)_p$	(D) $\left(\frac{\partial T}{\partial p}\right)_H$	
List II	1. μ_{JT}	2. T	3. –S	4. P	5. V

	A	**B**	**C**	**D**
(a)	5	1	2	4
(b)	5	3	2	4
(c)	3	5	2	1
(d)	5	3	2	1

Level – 2

More than one option is correct

1. Which of the following expression represents Gibbs-Helmholtz equation?

(a) $\Delta G^0 = \Delta H^0 + T\left[\frac{\partial(\Delta G^0)}{\partial T}\right]_p$ (b) $\left[\frac{\partial(\Delta G^0)}{\partial T}\right]_p = -\frac{\Delta H^0}{T^2}$

(c) $\left[\frac{\partial(\Delta G^0/T)}{\partial(1/T)}\right]_p = \Delta H^0$ (d) $\left[\frac{\partial(\Delta G^0/T)}{\partial T}\right]_p = \Delta H^0$

2. In an isothermal irreversible expansion of an ideal gas

(a) $\Delta U = 0$ (b) $-wq = nRT[1 - P_2/P_1]$

(c) $\Delta G \neq 0$ (d) all of these

3. The differential form of thermodynamic energies U, H and G can be represented by.

(a) dU = Tds – pdv (b) dH = Tds + Vdp

(c) dG = - SdT + Vdp (d) none of these

4. Which of the following mathematical relations are correct for an ideal gas?

(a) $\left(\frac{\partial H}{\partial V}\right)_T = 0$ (b) $\left(\frac{\partial H}{\partial p}\right)_T = 0$ (c) $C_p - C_V > R$ (d) $\left(\frac{\partial C_V}{\partial V}\right)_T = 0$

5. Which of these mathematical expressions is a perfect differential?

(a) $\int_1^2 dU = \Delta U$ (b) $\int_1^2 \delta W = \Delta W$ (c) $\int_1^2 \delta q = \Delta q$ (d) $dU = \delta q + \delta W$

6. An adiabatic process is one in which

(a) all energy is transferred as heat

(b) no energy is transferred as heat

(c) the temperature of a gas decreases in a reversible adiabatic expansion

(d) $dU \neq dW$

7. When the gas is ideal and the process is isothermal

(a) $p_1V_1 = p_2V_2$ (b) $U_1 = U_2$ (c) $H_1 \neq H_2$ (d) W = 0

8. Which of the following statements are correct?

(a) The work done by the system on the surroundings is negative.

(b) The work done on the system by the surroundings is positive.

(c) The heat absorbed by the system from the surroundings is positive.

(d) The heat absorbed by the surroundings from the system is negative.

9. Which of the following is a path function as well as an extensive property?

(a) Temperature (b) Internal energy

(c) Molar heat capacity (d) Heat capacity

10. For ideal diatomic gases,
(a) $C_p = (7/2)\ R$ (b) $C_p = (3/2)\ R$ (c) $C_V = (5/2)\ R$ (d) $C_V = (3/2)\ R$

11. When a solid melts there will be
(a) an increase in enthalpy (b) a decrease in free energy
(c) no change in enthalpy (d) a decrease in internal energy

12. Which of the following are thermodynamically stable?
(a) C (diamond) (b) C (graphite) (c) P_4 (white)(d) P_4 (red)

13. Which of the following are endothermic compounds?
(a) $N_2O_4(g)$ (b) $NO_2(g)$ (c) $N_2O_4(l)$ (d) $N_2H_4(l)$

14. The standard molar enthalpy of CO_2 is equal to
(a) the standard molar enthalpy of combustion of gaseous carbon
(b) the standard molar enthalpy of combustion of carbon (graphite)
(c) the sum of the standard molar enthalpies of formation of CO and O_2
(d) -394 kJ mol^{-1}

15. Which of the following statements are correct?
(a) The entropy of an isolated system increases in an irreversible process.
(b) The entropy of an isolated system remains unchanged in a reversible process.
(c) Entropy can never decrease.
(d) ΔS (system) as well as ΔS (surroundings) are negative quantities.

16. Which of the following statements are correct?
(a) When $\Delta G = 0$, the system is at equilibrium.
(b) When $\Delta G \angle 0$, the process will be spontaneous.
(c) When ΔG is negative, the process is said to be exergonic.
(d) When ΔG is positive, the process is said to be endergonic.

17. Which of the following relations are correct?
(a) $\Delta G = \Delta H - T\Delta S$ (b) $\Delta G = \Delta H + T\left[\frac{\partial(\Delta G)}{\partial T}\right]_p$
(c) $\Delta G = \Delta H + T\Delta S$ (d) $\Delta G = \Delta H + \Delta nRT$

18. In the following table, which of the options are correct?

	ΔH	ΔS	Nature of reaction
(a)	(-)	(+)	Spontaneous at all temperatures
(b)	(+)	(–)	Nonspontaneous regardless of temperature
(c)	(+)	(+)	Spontaneous only at high temperature
(d)	(-)	(-)	Spontaneous only at low temperature

Level – 3

FILL IN THE BLANKS

1. The total energy of one mole of an ideal monoatomic gas at 27^0 C is………. calories.

2. $C_p - C_v$ for an ideal gas is …………………

3. A system is said to be ……………..if it can neither exchange matter nor energy with the surroundings.

4. The heat content of the products is more than that of the reactants in an ……………. reaction.

5. Enthalpy is an ……………..property.

TRUE /FALSE

6. First law of thermodynamics is not adequate in predicting the direction of a process
7. Heat capacity of a diatomic gas is higher than that of a monoatomic gas.

Only one option is correct:

8. The difference between heats of reaction at constant pressure and constant volume for the reaction
$2C_6H_6\,(l) + 15O_2 \rightarrow 12CO_2\,(g) + 6H_2O\,(l)$ at 25^0C in kJ is:
(a) -7.43 (b) + 3.72 (c) -3.72 (d) + 7.43

9. For an endothermic reaction where ΔH represents the enthalpy of the reaction in kJ/mol, the minimum value for the energy of activation will be:
(a) less than ΔH (b) zero (c) more than ΔH (d) equal to ΔH

10. The ΔH^0_f for CO_2 (g), CO (g) and H_2O (g) are -393.5, - 110.5 and -241.8 kJ mol^{-1} respectively. The standard enthalpy change (in kJ mol^{-1}) for the reaction $CO_2\,(g) + H_2\,(g) \rightarrow CO\,(g) + H_2O\,(g)$ is:
(a) 524.1 (b) + 41.2 (c) -262.5 (d) 41.2

11. In thermodynamics, a process is called reversible when:
(a) surroundings and system change into each other
(b) there is no boundary between system and surroundings
(c) the surroundings are always in equilibrium with the system
(d) the system changes into the surroundings spontaneously

12. One mole of a non-ideal gas undergoes a change of state (2.0 atm, 3.0 L, 95K) → (4.0 atm, 5.0L, 245 K) with a change in internal energy, ΔU = 30.0 L-atm. The change in enthalpy (ΔH) of the process in L-atm is:
(a) 40.0 (b) 42.3 (c) 44.0
(d) not defined, because pressure is not constant

13. Which of the reaction defines ΔH^0_f?
(a) $C_{(diamond)} + O_2(g) \longrightarrow CO_2(g)$ (b) $\frac{1}{2}H_2(g) + \frac{1}{2}F_2(g) \longrightarrow HF(g)$
(c) $N_2(s) + 3H_2(g) \longrightarrow 2NH_3(g)$ (d) $CO(g) + \frac{1}{2}O_2(g) \longrightarrow CO_2(g)$

14. Spontaneous adsorption of a gas on solid surface is an exothermic process because:
(a) ΔH increases for system (b) ΔS increases for gas
(c) ΔS decreases for gas (d) ΔG increases for gas

15. ΔH_{vap} = 30 kJ/mol and ΔS_{vap} = 75 $Jmol^{-1}K^{-1}$. Find temperature of vapour, at one atmosphere.
(a) 400K (b) 350K (c) 298K (d) 250K

16. 2 mole of an ideal gas expanded isothermally and reversibly from 1 L to 10 L at 300 K. What is the enthalpy change?
(a) 4.98 kJ (b) 11.47 kJ (c) -11.47 kJ (d) 0 kJ

17. When one mole of monoatomic ideal gas at TK undergoes adiabatic change under a constant external pressure of 1 atm changes volume from 1 L to 2 L. The final temperature in Kelvin would be:
(a) $\frac{T}{2^{2/3}}$ (b) $T + \frac{2}{3 \times 0.0821}$ (c) T (d) $T - \frac{2}{3 \times 0.0821}$

18. A monoatomic ideal gas undergoes a process in which the ratio of P to V at any instant is constant and equals to 1. What is the molar heat capacity of the gas?
(a) $\frac{4R}{2}$ (b) $\frac{3R}{2}$ (c) $\frac{5R}{2}$ (d) 0

19. The direct conversion of A to B is difficult, hence it is carried out by the following shown path

$$\begin{tikzcd} C \arrow[r] & D \arrow[d] \\ A \arrow[u] & B \end{tikzcd}$$

Given $\Delta S_{(A \to C)}$ = 50 eu
$\Delta S_{(C \to D)}$ = 30 eu
$\Delta S_{(B \to D)}$ = 20 eu
where eu is entropy unit, then $\Delta S_{(A \to B)}$ is:

(a) +100 eu (b) +60 eu (c) -100 eu (d) -60 eu

20. $N_2 + 3H_2 \rightleftharpoons 2NH_3$

Which is correct statement if N_2 is added at equilibrium condition?

(a) The equilibrium will shift to forward direction because according to IInd law of thermodynamics the entropy must increases in the direction of spontaneous reaction.

(b) The condition for equilibrium is $G_{N_2} + 3G_{H_2} = 2G_{NH_3}$ where G is Gibbs free energy per mole of the gaseous species measured at the partial pressure. The condition of equilibrium is unaffected by the use of catalyst, which increases the rate of both the forward and backward reactions to the same extent.

(c) The catalyst will increase the rate of forward reaction by α and that of backward reaction by β.

(d) Catalyst will not alter the rate of either of the reaction.

21. The value of $\log_{10}K$ for a reaction $A \rightleftharpoons B$ is (Given: $\Delta_rH^0_{298K}$ = -54.07 kJ mol^{-1}, $\Delta_rS^0_{298K}$ = 10$JK^{-1}mol^{-1}$ and R = 8.314 $JK^{-1}mol^{-1}$; 2.303 × 8.314 × 298 = 5705)

(a) 5 (b) 10 (c) 95 (d) 100

22. For the process $H_2O(l)$ (1 bar, 273 K) → H_2O (g) (1 bar, 373 K), the correct set of thermodynamic parameters is:

(a) $\Delta G = 0, \Delta S = +Ve$ (b) $\Delta G = 0, \Delta S = -ve$

(c) $\Delta G = +ve, \Delta S = 0$ (d) $\Delta G = -ve, \Delta S = +ve$

More than one options are correct:

23. Identify the intensive quantities from the following:

(a) enthalpy (b) temperature (c) volume (d) refractive index

24. The following is (are) endothermic reaction (s):

(a) combustion of methane (b) decomposition of water

(c) dehydrogenation of ethane to ethylene

(d) conversion of graphite to diamond

25. Which one of the following statement is false?

(a) Work is a state function. (b) Temperature is a state function.

(c) Change in the state is completely defined when the initial and final states are specified.

(d) Work appears at the boundary of the system

Level - 1
Answer key

Q.	Ans.	Q.	Ans.	Q.	Ans.	Q.	Ans.
1.	B	11.	B	21.	C	31.	B
2.	B	12.	A	22.	D	32.	C
3.	B	13.	B	23.	C	33.	B
4.	D	14.	D	24.	A	34.	C
5.	B	15.	B	25.	D	35.	D
6.	B	16.	D	26.	B		
7.	D	17.	B	27.	A		
8.	C	18.	D	28.	B		
9.	C	19.	A	29.	D		
10.	A	20.	B	30.	C		

SOLUTION

1. In an exothermic reaction $H_R > H_p \text{ or } H_p < H_R$.

2. $\Delta H = \Delta E + P\,\Delta V$.

3. $\Delta H = \Delta E + \Delta n_g RT$.

4. In $H_2O(\boldsymbol{l}) \rightarrow H_2O(g) \rightarrow$ heat is absorbed.
Hence $\Delta H_f^0\left[H_2O(g)\right] < \Delta H_f^0\left[H_2O(1)\right]$

5. Less the heat of neutralisation, weaker is the acid.

6. $\Delta S = q_{rev} / T$.

7. For a reversible process, $\Delta S_{sys} + \Delta S_{surr} = 0$.

8. 1 calorie = 4.184 j, 1 erg = 10^{-7} joule.

9. By definition of 3rd law of thermodynamics.

10. Dilution of conc. H_2SO_4 is an exothermic process.

11. NH_4OH is a weak base. Heat of neutralisation < 13.7 kcal.

12. Suppose heat evolved in 1st case is Q_1 and that in the 2nd case it is Q_2.

Then $Q_2 = \frac{1}{2}Q_1.$

But $Q_1 = 1000\ T_1$ and $Q_2 = 500\,T_2$

$\therefore 500\,T_2 = \frac{1}{2} \times 1000\ T_1$ i.e. $T_2 = T_1$.

13. 1 MH_2SO_4 = 2 g eq. of H_2SO_4 .

Hence y = 2x or $x = \frac{1}{2}y$.

14. All values are equivalent.

15. For the formation of 1 mole of HCl from elements, $\Delta H_f^0 = -22\,\text{kcal}.$

16. $\Delta G^0 = -RT\ \text{In}\,K_p$ or in $K_p = -\dfrac{\Delta G^0}{RT}$ Or $K_p = e^{\Delta G^0} / RT$

17. For $C + \frac{1}{2}O_2 \rightarrow CO$, operate eqn. (i) $-\frac{1}{2}$eqn.

(ii) $\Delta H = -x - \frac{1}{2}(-y) = -x + \frac{y}{2} = \frac{y-2x}{2}.$

18. Indeterminate unless C-C bond energy is known.

19. For $S+O_2 \rightarrow SO_2$, operate eqn. (i) - eqn (ii) .This gives ΔH = y – 2x.

20. $\Delta n_g = n_p - n_r = 3 - 6 = -3$

$\therefore \quad \Delta H = \Delta E + \Delta n_g\ RT$ or $\Delta H - \Delta E = \Delta n_g RT = -3\,RT$.

21. Since internal energy is a state function and the system returns to original state, DETAE = 0 (i,e. for a cyclic process ΔE = 0)

22. 50 ml of 1 M KOH + 50 ml of 0.5 M H_2SO_4 will involve complete neutralisation.

23. 250 ml of 4 N NaOH ≅ 500 ml of 2 N NaOH. This will completely neutralise 500 ml of 2 N HCl.
Heat evolved from 1000 ml of 1 N HCl = x (Given)
∴ Heat evolved from 500 ml of 2 N HCl = x

24. Eqn. (i) +Eqn. (ii) + Eqn. (iii) gives, X = 131—282—242 = —393 kJ.

25. $$\Delta H_{\text{reaction}} = \Delta H_f^0 \left(N_2O_4\right) - 2\,\Delta H_f^0 \left(NO_2\right)$$
$$= 2 - 2(8) = -14 \text{ kcal.}$$

26. Eqn. (i) – Eqn. (ii) gives the required result.

27. Energy absorbed in the dissociation of 1 mole of H_2O = 2 × 109 = 218 kcal
This will be the energy released when 1 mole of H_2O is formed.

28. For isothermal expansion of ideal gas, $\Delta E = 0$.

29. At constant temperature
$$\Delta S = nR \text{ in} \frac{V_2}{V_1} = 2.303\, nR \log \frac{V_2}{V_1} = 2.303 \times 2 \times 2 \log \frac{20}{2} = 9.2 \text{ cal K}^{-1} \text{ mol}^{-1}$$

30. H =U + PV .As pressure is not constant,
$$\Delta H = H_2 - H_1 = (U_2 + P_2V_2) - (U_1 + P_1V_1)$$
$$= (U_2 - U_1) + (P_2V_2 - P_1V_1) = 30 + 4 \times 5 - 2 \times 3 = 44 \text{ L atm}$$

31. More cis-pentene is formed to restore the equilibrium.

32. $$NaOH + HCl \rightarrow NaCl + H_2O \text{means}$$
$$H^+ + OH^- \rightarrow H_2O, \Delta H = -57.3 \text{kJ}$$
Hence $H_2O \rightarrow H^+ + OH^-$, $\Delta H = +57.3\,\text{kJ}$

33. q_2 is heat of neutralization of strong acid with strong base and q_1 is that of weak acid HA with strong base. The difference gives the heat of dissocitation of HA, i,e., $\Delta H = \Delta H_2 - \Delta H_1$ = (-q)- (-q_1) = q_1 - q_2

34. Volume of 1 mole of H_2O at 373 K and 1 atm
(V_1) = 18 cm^3= 0.018L
Volume of 1 mole of H_2O vapour at 373 K and 1 atm (PV=RT)
$$V_2 = \frac{RT}{P} = \frac{0.0821 \times 373}{1} 30.62 \text{L}$$

$w = -P(V_2 - V_1) = -1(30.62-0.018) = -30.6$ L atm.
$= -30.6 \times 101.3 = -3100$ J.

35. From thermo dynamics, $dG = Vdp - SdT$

At constant T, $dT = 0$ so that $\left(\frac{\partial G}{\partial P}\right)_T = V$

At constant P, $dP = 0$ so that $\left(\frac{\partial G}{\partial T}\right)_p = -S$

Also $\mu_{JT} = \left(\frac{\partial T}{\partial P}\right)_H$.

Level – 2
Answer key

Q.	ANS.	Q.	ANS.	Q.	ANS.
1.	a, c	2.	a, b	3.	a, b, c
4.	a, b, d	5.	a, d	6.	b, c
7.	a, b	8.	a, b, c, d	9.	b, d
10.	a, c	11.	a, b	12.	b, c
13.	a, b, d	14.	b, d	15.	a, b, c
16.	a, b, c, d	17.	a, b	18.	a, b, c, d

Level – 3

FILL IN THE BLANKS

1. 900 2. R 3. isolated 4. endothermic 5. extensive

TRUE /FALSE

6. **True**: It only tells that if a process occurs the heat gained by one end would be exactly equal to lost by the other. It does not predict the direction.

7. **False**: $\frac{C_p}{C_v}$ for monoatomic gas = 1.66 and $\frac{C_p}{C_v}$ for diatomic gas = 1.40

(*Only one option is correct:)*

8. $\Delta H = \Delta E + \Delta nRT$
Here, $\Delta n = 12 - 15 = -3$

$\therefore \quad \Delta H - \Delta E = -3 \times 8.314 \times 298 = -7.43$ kJ

9. $\Delta H = (E_a)_f - (E_a)_b$
For endothermic reaction, ΔH is positive. Thus the minimum value for the energy of activation will be more than ΔH.

10. For reaction: $CO_2(g)H_2(g) \longrightarrow CO(g) + H_2O(g), \ \Delta H = [?]$

$$\Delta H = \left[\left(\Delta H_f \text{ of } CO(g) + \Delta H_f \text{ of } H_2O(g) - \left(\Delta H_f \text{ of } CO_2(g) + \Delta H_f \text{ of } H_2(g)\right)\right)\right]$$

$$= \left[(-110.5) + (-241.8) - (393.5 + 0)\right] \text{kJ} \qquad \left(\because \Delta H_f \text{ of } O_2 = 0\right)$$

$$= -352.3 + 393.5 = +41.2 \text{kJ}$$

11. In thermodynamics, a process is called reversible when the surroundings are always in equilibrium with the system

12. $\Delta H = \Delta U + \Delta n R\Delta T \qquad (\therefore \Delta U = \Delta E)$
$\Delta n = 1$ mole, $\Delta T = (245 - 95) = 150$K
R = 0.0821 L atm/K/mol
$\Delta U = 30.0$L-atm
$\therefore \quad \Delta H = 30 + 1 \times 0.0821 \times 150 = 42.3$ L-atm

13. The amount of heat either evolved or absorbed when one gram mole of a substance is formed from its constituent elements, is known as the standard heat of formations (ΔH^0_f).
For standard state temperature is 25^0C or 298K and pressure of gaseous substance is one atmosphere.
Thus in given thermochemical equation 'b' represents the standard heat of formation of HF.

$$\frac{1}{2}H_2(g) + \frac{1}{2}F_2(g) \longrightarrow HF(g), \quad \Delta H^0{}_f = ?$$

(standard heat of formation of HF(g))

14. For spontaneous adsorption process, standard Gibb's free energy (ΔG) must be negative as well as the degree of randomness of gas molecule on the surface of solid decreases. For exothermic process, ΔH must be negative. Hence, with the help of following equation: $\Delta H = \Delta G + T\Delta S$
TΔS is negative.
Thus, during this adsorption ΔS decreases.

15. Given that,
$\Delta H_{vaps} = 30$ kJ/mol $= 30 \times 10^3$ J/mol
$\Delta S_{vaps} = 75$ J/mol
We know that
$$\Delta G = \Delta H - T\Delta S$$

At equilibrium, $\Delta G = 0$

$\therefore$ $\Delta H = T\Delta S$ or $30 \times 10^3 = T \times 75$

$$T = \frac{30 \times 10^3}{75} = 400K$$

16. $\because$ $H = E + PV$ and $\Delta H = \Delta E + P\Delta V$

$P\Delta V = nRT$

$\therefore$ $\Delta H = \Delta E + nR\Delta T$

For isothermal and reversible process $\Delta T = 0$

$\therefore$ $\Delta H = \Delta E + 0,$ $\because$ $\Delta E = 0$

$\therefore$ ΔH is also equal to zero.

17. For adiabatic change $\Delta E = \Delta W$

$\Delta E = nC_v (T_2 - T_1)$

$\Delta W = -P (V_2 - V_t)$

$\therefore$ $nC_v(T_2 - T_\gamma) = -P (V_2 - V_t) = -1 (2 - 1)$

$n \times R/\gamma - 1 \times (T_2 - T) = -1$

$n = 1, \gamma = 5/3$ for monoatomic gas, $R = 0.0821$ L-atm/K-mol

$$1 \times \frac{0.0821}{5/3 - 1} \times (T_2 - T) = -1 \quad \text{or} \quad T_2 = T - \frac{2}{3 \times 0.0821}$$

18. The molar heat capacity for any process is given by a following expression $C = C_V + \frac{R}{1-\gamma}$ when $PV^\gamma = \text{constant}$ and $C_P/C_V = \gamma$

Here $\frac{P}{V} = 1$ i.e., $PV^{-1} = \text{constant}$

$$\therefore \quad C = \frac{3}{2}R + \frac{R}{1-(-1)} = \frac{3}{2}R + \frac{R}{2} = \frac{4}{2}R$$

19. $$\begin{tikzcd} C \arrow[r] & D \arrow[d] \\ A \arrow[u] & B \end{tikzcd}$$

Given $\Delta S_{(A \to C)} = 50$ eu

$\Delta S_{(C \to D)} = 30$ eu

$\Delta S_{(B \to D)} = 20$ eu

where eu is entropy unit.

Therefore,

$$\Delta S_{(A \to B)} = \Delta S_{(A \to C)} + \Delta S_{(C \to D)} + \Delta S_{(D \to B)}$$
$$= \Delta S_{(A \to C)} + \Delta S_{(C \to D)} - \Delta S_{(B \to D)}$$
$$= 50 + 30 - 20 = 60 \text{ eu}$$

20. $N_2 + 3H_2 \rightleftharpoons 2NH_3$

K_c (Eq. constant) = $\dfrac{[NH_3]^2}{[N_2][H_2]^3}$, $K_p = \dfrac{(P_{NH_3})^2}{P_{N_2} \times (P_{H_2})^3}$

K_p or K_c remains constant for above reaction at constant temperature. Although in presence of catalyst rate of forward and backward reaction is increased in same order (extent) due to decreasing the activation energy of both reaction. So the equilibrium is established in short time i.e., catalyst is able to increase the concentration of reactants and products in same order, so the value of K_c or K_p remains constant. Hence equilibrium state is not effected in presence of catalyst. Hence, at equilibrium $\Delta G = 0$

$\because$ $\Delta G = 2G$ of NH_3 – (G of H_2 + 3 × G of NH_3)

$\therefore$ $G_{N_2} + 3G_{H_2} = 2G_{NH_3}$

21. $A \rightleftharpoons B$

$\Delta G^0 = \Delta H^0 - T\Delta S^0$

$\Delta G^0 = -2303\ RT \log K$

$$\log K = \frac{\Delta H^0 - T\Delta S^0}{-2.303\ RT} = \frac{-54.07 \times 10^3 - 298 \times 10}{-2.303 \times 8.314 \times 298} = \frac{-57050}{-5705} = 10$$

22. $H_2O(l)$ and $H_2O(g)$ both exist together at same temperature and pressure, suggests the state of equilibrium

Hence, $\Delta G = 0$

and conversion of liquid into gas increases disorderness, hence entropy ΔS = +ve.

(*More than one options are correct:)*

23. Those physical properties which are not based upon the mass are known as intensive properties.

24. Factual question

25. Work and temperature are not state functions as their value are not specific for a state.

New Questions

9. Heat produced in calories by the combustion of one gram of carbon is called

(a) Heat of combustion of carbon
(b) Heat of formation of carbon
(c) Calorific value of carbon
(d) Heat of production of carbon

10. Conditions of standard state used in thermochemistry is

(a) 0^oC and 1 atm (b) 20^oC and 1 atm
(c) 25^oC and 1 atm (d) $0K$ and 1 atm

11. The temperature of the system decreases in an **[KCET 2005]**

(a) Adiabatic compression (b) Isothermal compression
(c) Isothermal expansion (d) Adiabatic expansion

12. For the isothermal expansion of an ideal gas

(a) E and H increases
(b) E increases but H decreases
(c) H increases but E decreases
(d) E and H are unaltered

13. If a refrigerator's door is opened, then we get **[CPMT 1980]**

(a) Room heated
(b) Room cooled
(c) More amount of heat is passed out
(d) No effect on room

14. The cooling in refrigerator is due to **[KCET 2005]**

(a) Reaction of the refrigerator gas
(b) Expansion of ice
(c) The expansion of the gas in the refrigerator
(d) The work of the compressor

15. Point out the wrong statement in relation to enthalpy

(a) It is a state function
(b) It is an intensive property
(c) It is independent of the path followed for the change
(d) Its value depends upon the amount of substance in the system

16. Which of the following is zero for an isochoric process

(a) dP (b) dV
(c) dT (d) dE

17. Mark the *correct* statement **[MP PET 1997]**

(a) For a chemical reaction to be feasible, ΔG should be zero
(b) Entropy is a measure of order in a system
(c) For a chemical reaction to be feasible, ΔG should be positive
(d) The total energy of an isolated system is constant

18. In an isochoric process the increase in internal energy is **[MP PMT 1997]**

(a) Equal to the heat absorbed
(b) Equal to the heat evolved
(c) Equal to the work done
(d) Equal to the sum of the heat absorbed and work done

19. It is general principle that the less energy a system contains, it is **[MH CET 1999]**

(a) Less stable (b) More stable
(c) Unstable (d) More unstable

20. Internal energy is an example of **[Pb. PMT 2000]**

(a) Path function (b) State function
(c) Both (a) and (b) (d) None of these

21. The process, in which no heat enters or leaves the system, is termed as **[Pb. PMT 1999; Kerala (Med.) 2002; J & K 2005]**

(a) Isochoric (b) Isobaric
(c) Isothermal (d) Adiabatic

22. The intensive property among these quantities is **[KCET 2002]**

(a) Enthalpy (b) Mass/volume
(c) Mass (d) Volume

23. In thermodynamics which one of the following is not an intensive property **[Kerala (Med.) 2002]**

(a) Pressure (b) Density
(c) Volume (d) Temperature

24. If in a container neither mass and nor heat exchange occurs then it constitutes a **[MP PMT 1993; AFMC 2003]**

(a) Closed system (b) Open system
(c) Isolated system (d) Imaginary system

25. Which of the following is not a state function **[DCE 2002]**

(a) ΔS (b) ΔG
(c) ΔH (d) ΔQ

26. Which of the following is true for an adiabatic process **[DCE 2002; MP PET 1995, 98, 2004; CPMT 1990; MP PMT 1998, 2002]**

(a) $\Delta H = 0$ (b) $\Delta W = 0$
(c) $\Delta Q = 0$ (d) $\Delta V = 0$

27. Which of the following is not a state function **[MH CET 2004; AIIMS 2001]**

(a) Internal energy (b) Enthalpy
(c) Work (d) Entropy

28. Among them intensive property is **[AFMC 2004]**

(a) Mass (b) Volume

(c) Surface tension (d) Enthalpy

First law of thermodynamics and Hess law

1. The first law of thermodynamics is only

(a) The law of conservation of energy

(b) The law of conservation of mass

(c) The law of conservation of momentum

(d) Both (a) and (b)

2. A mixture of two moles of carbon monoxide and one mole of oxygen, in a closed vessel is ignited to convert the carbon monoxide to carbon dioxide. If ΔH is the enthalpy change and ΔE is the change in internal energy, then **[KCET 2005]**

(a) $\Delta H > \Delta E$

(b) $\Delta H < \Delta E$

(c) $\Delta H = \Delta E$

(d) The relationship depends on the capacity of the vessel

3. Which of the following is always negative for exothermic reaction? **[BCECE 2005]**

(a) ΔH (b) ΔS

(c) ΔG (d) None of these

4. The relation between ΔE and ΔH is

[MP PET 1992; MP PMT 1996; MP PET/PMT 1998]

(a) $\Delta H = \Delta E - P\,\Delta V$ (b) $\Delta H = \Delta E + P\,\Delta V$

(c) $\Delta E = \Delta V + \Delta H$ (d) $\Delta E = \Delta H + P\,\Delta V$

5. At constant T and P, which one of the following statements is correct for the reaction,

$$CO(g) + \frac{1}{2}O_2(g) \rightarrow CO_2(g)$$

[AIIMS 1982, 83; KCET 1988; BHU 1995; MP PET 1997, 99]

(a) ΔH is independent of the physical state of the reactants of that compound

(b) $\Delta H > \Delta E$

(c) $\Delta H < \Delta E$

(d) $\Delta H = \Delta E$

6. For the reaction of one mole of zinc dust with one mole of sulphuric acid in a bomb calorimeter, ΔU and w correspond to **[AIIMS 2005]**

(a) $\Delta U < 0, w = 0$ (b) $\Delta U = 0, w < 0$

(c) $\Delta U > 0, w = 0$ (d) $\Delta U < 0, w > 0$

7. Which is not the correct relation between enthalpy (ΔH) and intrinsic energy (ΔE) **[EAMCET 1992]**

(a) $\Delta H = \Delta E + P\,\Delta V$ (b) $\Delta H = \Delta E + nRT$

(c) $\Delta H = \Delta E - P\,\Delta V$ (d) $\Delta E = \Delta H - P\,\Delta V$

8. The law of Lavoisier and Laplace illustrates

[KCET 1989]

(a) The principle of conservation of energy

(b) Equivalence of mechanical and thermal energy

(c) The principle of conservation of matter

(d) Equivalence of mechanical and chemical energy

9. For the reaction $N_2 + 3H_2 \rightleftharpoons 2NH_3; \Delta H =$

[Roorkee 2000; CBSE PMT 1991, 2002]

(a) $\Delta E - RT$ (b) $\Delta E - 2RT$

(c) $\Delta E + RT$ (d) $\Delta E + 2RT$

10. If ΔH is the change in enthalpy and ΔE the change in internal energy accompanying a gaseous reaction

[KCET 1989; CBSE PMT 1990]

(a) ΔH is always greater than ΔE

(b) $\Delta H < \Delta E$ only if the number of moles of the products is greater than the number of the reactants

(c) ΔH is always less than ΔE

(d) $\Delta H < \Delta E$ only if the number of moles of the products is less than the number of moles of the reactants

11. "The resultant heat change in a reaction is the same whether it takes place in one or several stages." This statement is called **[MP PMT/PET 1988; MP PMT 1989]**

(a) Lavoisier and Laplace law

(b) Hess's law

(c) Joule's law

(d) Le–chatelier's principle

12. Hess's law of constant heat summation in based on

[MP PET 2001]

(a) $E = mc^2$

(b) Conservation of mass

(c) First law of thermodynamics

(d) None of the above

13. Consider the reaction : $N_2 + 3H_2 \rightarrow 2NH_3$ carried out at constant temperature and pressure. If ΔH and ΔU are the enthalpy and internal energy changes for the reaction, which of the following expression is true

[AIEEE 2005]

(a) $\Delta H = 0$ (b) $\Delta H = \Delta U$

(c) $\Delta H < \Delta U$ (d) $\Delta H > \Delta U$

14. Which of the following is the correct equation

[CBSE PMT 1996]

(a) $\Delta U = \Delta Q - W$ (b) $\Delta W = \Delta U + \Delta Q$

(c) $\Delta U = \Delta W + \Delta Q$ (d) None of these

15. Hess law is applicable for the determination of heat of

[AIIMS 1998; Pb. PET/PMT 1999]

(a) Reaction (b) Formation

(c) Transition (d) All of these

16. Enthalpy for the reaction $C + O_2 \rightarrow CO_2$ is

[DPMT 1987, 91]

(a) Positive (b) Negative

(c) Zero (d) None

17. During an isothermal expansion of an ideal gas its

[CBSE PMT 1991]

(a) Internal energy increases

(b) Enthalpy decreases

(c) Enthalpy remains unaffected

(d) Enthalpy reduces to zero

18. The work done in ergs for the reversible expansion of one mole of an ideal gas from a volume of 10 litres to 20 litres at $25^0 C$ is **[CMC Vellore 1991]**

(a) $2.303 \times 298 \times 0.082 \log 2$

(b) $298 \times 10^7 \times 8.31 \times 2.303 \log 2$

(c) $2.303 \times 298 \times 0.082 \log 0.5$

(d) $8.31 \times 10^7 \times 298 - 2.303 \log 0.5$

(e) $2.303 \times 298 \times 2 \log 2$

19. The law of conservation of energy states that

[NCERT 1984]

(a) The internal energy of a system is constant

(b) The heat content of a system is constant

(c) Energy is neither created nor destroyed

(d) There is an equivalence between energy and mass

20. The enthalpies of the elements in their standard states are assumed to be

(a) Zero at 298 K

(b) Unit at 298 K

(c) Zero at all temperatures

(d) Zero at 273 K

21. The heat Q for a reaction at constant volume is equal to

(a) $H_P - H_R$ (b) $H_R - H_P$

(c) $E_P - E_R$ (d) None of these

22. Which of the following expressions represents the first law of thermodynamics

[MP PET 1996, 2000; AFMC 1997; BHU 1999; AMU 2000; KCET (Med.) 2000, 01; CBSE PMT 2000; MP PMT 2002]

(a) $\Delta E = -q + W$ (b) $\Delta E = q - W$

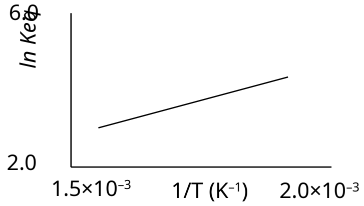
(c) $\Delta E = q + W$ (d) $\Delta E = -q - W$

23. In a reversible isothermal process, the change in internal energy is

(a) Zero (b) Positive

(c) Negative (d) None of these

24. A schematic plot of lnK_{eq} versus inverse of temperature for a reaction is shown below



The reaction must be **[AIEEE 2005]**

(a) Exothermic

(b) Endothermic

(c) One with negligible enthalpy change

(d) Highly spontaneous at ordinary temperature

25. Hess law of heat summation includes **[AFMC 1992]**

(a) Initial reactants only

(b) Initial reactants and final products

(c) Final products only

(d) Intermediates only

26. An ideal gas at constant temperature and pressure expands, then its **[BHU 1998]**

(a) Internal energy remains same

(b) Internal energy decreases

(c) Internal energy increases

(d) Entropy first increases and then decreases

27. The internal energy of a substance

[KCET 1998; AFMC 2001; AIIMS 2001]

(a) Increases with increase in temperature

(b) Decreases with increase in temperature

(c) Can be calculated by the relation $E = mc^2$

(d) Remains unaffected with change in temperature

28. The relation between change in internal energy (ΔE), change in enthalpy (ΔH) and work done (*W*) is represented as **[AFMC 1999]**

(a) $\Delta H = \Delta E + W$ (b) $W = \Delta E - \Delta H$

(c) $\Delta E = W - \Delta H$ (d) $\Delta E = \Delta H + W$

29. The enthalpy of neutralization of which of the following acids and bases is nearly $-13.6\ Kcal$ **[Roorkee 1999]**

(a) *HCN* and *NaOH* (b) *HCl* and *KOH*

(c) *HCl* and *NaOH* (d) *HCl* and NH_4OH

30. Work done during isothermal expansion of one mole of an ideal gas from 10 *atm* to 1 *atm* at 300 *K* is (Gas constant = 2) **[AIIMS 2000]**

(a) 938.8 *cal*. (b) 1138.8 *cal*.

(c) 1381.8 *cal*. (d) 1581.8 *cal*.

31. Joule-Thomson expansion is **[JIPMER 2000]**

(a) Isobaric (b) Isoenthalpic

(c) Isothermal (d) None of these

32. In which of the following $\Delta E = \Delta H$ **[MP PMT 2001]**

(a) $N_2O_4(g) \rightleftharpoons 2NO_2(g)$

(b) $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$

(c) $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$

(d) $H_2(g) + \frac{1}{2}O_2(g) \rightleftharpoons H_2O(l)$

33. In an adiabatic expansion of an ideal gas **[KCET (Med.) 2001; MH CET 2000]**

(a) $W = -\Delta E$ (b) $W = \Delta E$

(c) $\Delta E = 0$ (d) $W = 0$

34. For the reaction $CH_3COOH\ (l) + 2O_2(g) \rightleftharpoons 2CO_2(g) + 2H_2O(l)$ at $25^\circ C$ and 1 *atm*. pressure, $\Delta H = -874 kJ$. Then the change in internal energy (ΔE) is .... **[Orissa JEE 2002]**

(a) – 874 *kJ* (b) – 871.53 *kJ*

(c) – 876.47 *kJ* (d) + 874 *kJ*

35. In a closed insulated container, a liquid is stirred with a paddle to increase its temperature. In this process, which of the following is true **[CBSE PMT 2002]**

(a) $\Delta E = W = Q = 0$ (b) $\Delta E \neq 0, Q = W = 0$

(c) $\Delta E = W \neq 0, Q = 0$ (d) $\Delta E = Q \neq 0, W = 0$

36. Hess law is based on **[MH CET 2002]**

(a) Law of conservation of mass

(b) Law of conservation of energy

(c) Enthalpy is a state function

(d) None of these

37. For the reaction, $C_3H_8(g) + 5O_2(g) \rightarrow 3CO_2(g) + 4H_2O(l)$ at constant temperature, $\Delta H - \Delta E$ is **[CBSE PMT 2003]**

(a) – *RT* (b) + *RT*

(c) – 3*RT* (d) + 3*RT*

38. According to Hess's law, the heat of reaction depends upon **[MP PMT 2003]**

(a) Initial condition of reactants

(b) Initial and final conditions of reactants

(c) Intermediate path of the reaction

(d) End conditions of reactants

39. The value of $\Delta H - \Delta E$ for the following reaction at $27^\circ C$ will be $2NH_3(g) \rightarrow N_2(g) + 3H_2(g)$ **[Kerala (Med.) 2002]**

(a) $8.314 \times 273 \times (-2)$ (b) $8.314 \times 300 \times (-2)$

(c) $8.314 \times 27 \times (-2)$ (d) $8.314 \times 300 \times (2)$

40. For which of the following $\Delta E = \Delta H$ **[MP PET 2003]**

(a) $N_2O_4(g) \rightleftharpoons 2NO_2(g)$

(b) $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$

(c) $H_2(g) + Cl_2(g) \rightleftharpoons 2HCl\ (g)$

(d) $H_2(g) + \frac{1}{2}O_2(g) \rightleftharpoons H_2O(l)$

41. One mole of an ideal gas is allowed to expand freely and adiabatically into vacuum until its volume has doubled. A statement which is not true concerning this expression is **[Pb. PMT 1998]**

(a) $\Delta H = 0$ (b) $\Delta S = 0$

(c) $\Delta E = 0$ (d) $W = 0$

42. At $27^\circ C$, one mole of an ideal gas is compressed isothermally and reversibly from a pressure of 2 *atm* to 10 *atm*. The values of ΔE and *q* are $(R = 2)$ **[BHU 2001]**

(a) 0, – 965.84 *cal*

(b) – 965.84 *cal*, + 965.84 *cal*

(c) + 865.58 *cal*, – 865.58 *cal*

(d) – 865.58 *cal*, – 865.58 *cal*

43. The work done by a system is 8 *joule,* when 40 *joule* heat is supplied to it. What is the increase in internal energy of system **[BHU 2001]**

(a) 25 *J* (b) 30 *J*

(c) 32 *J* (d) 28 *J*

44. A system absorb 600*J* of heat and work equivalent to 300*J* on its surroundings. The change in internal energy is

[Pb. PMT 2004]

(a) 300 *J* (b) 400 *J*

(c) 500 *J* (d) 600 *J*

45. Work done during isothermal expansion of one mole of an ideal gas from 10 atom. to 1 atm at 300K is **[BHU 2004]**

(a) 4938.8 *J* (b) 4138.8 *J*

(c) 5744.1 *J* (d) 6257.2 *J*

46. If gas, at constant temperature and pressure expands then its

[MH CET 2003]

(a) Entropy increases and then decreases

(b) Internal energy increases

(c) Internal energy remains the same

(d) Internal energy decreases

47. For the reaction

$PCl_5(g) \rightarrow PCl_3(g) + Cl_2(g)$ **[MH CET 2004]**

(a) $\Delta H = \Delta E$ (b) $\Delta H > \Delta E$

(c) $\Delta H < \Delta E$ (d) None of these

48. Enthalpy (H) is equal to **[MH CET 2004]**

(a) Internal energy (E)

(b) Product of pressure (P) and volume (V) of gas

(c) Internal energy (E)+PV

(d) Work (W) done by a system

49. ΔE^o of combustion of isobutylene is $-X\ kJ\ mol^{-1}$. The value of ΔH^o is **[DCE 2004]**

(a) $= \Delta E^o$ (b) $> \Delta E^o$

(c) $= 0$ (d) $< \Delta E^o$

50. One mole of an ideal gas is allowed to expand reversibly and adibatically from a temperature of $27^o C$. If the work done during the process is $3\,kJ$, then final temperature of the gas is $(C_V = 20 J / K)$

[Pb. CET 2002]

(a) 100 *K* (b) 150 *K*

(c) 195 *K* (d) 255 *K*

51. Which of the following is correct regarding the internal energy of a substance **[Pb. CET 2002]**

(a) It is a state function

(b) It increases with increase in temperature

(c) It can be calculated by experiment

(d) It remains unaffected with change in temperature

52. For the gaseous reaction,

$N_2O_4 \rightarrow 2NO_2$ **[Pb. CET 2003]**

(a) $\Delta H < \Delta E$ (b) $\Delta H = \Delta E$

(c) $\Delta H = 0$ (d) $\Delta H > \Delta E$

53. $2C + O_2 \rightarrow 2CO\,;\ \Delta H = -220 kJ$

Which of the following statement is correct for this reaction

[BVP 2004]

(a) Heat of combustion of carbon is 110 *kJ*

(b) Reaction is exothermic

(c) Reaction needs no initiation

(d) All of these are correct

54. An ideal gas expands in volume from $1 \times 10^{-3} m^3$ to $1 \times 10^{-2} m^3$ at 300 *K* against a constant pressure of $1 \times 10^5\ Nm^{-2}$. The work done is **[AIEEE 2004]**

(a) 270 *kJ* (b) –900 *kJ*

(c) –900 *J* (d) 900 *kJ*

55. Internal energy is **[AFMC 2004]**

(a) Partly potential and partly kinetic

(b) Totally kinetic

(c) Totally potential

(d) None of these

56. For which of the reaction $\Delta H = \Delta E$ **[MP PET 2004]**

(a) $N_2 + 3H_2 \rightleftharpoons 2NH_3$ (b) $N_2 + O_2 \rightarrow 2NO$

(c) $2Na + Cl_2 \rightarrow 2NaCl$ (d) $PCl_5 \rightarrow PCl_3 + Cl_2$

57. The work done during the expansion of a gas from a volume of $4 dm^3$ to $6 dm^3$ against a constant external pressure of $3 atm$ is ($1 L\ atm = 101.32 J$)

[CBSE PMT 2004]

(a) + 304 *J* (b) –304 *J*

(c) – 6 *J* (d) –608 *J*

58. For the reaction, $A_{(s)} + 2B_{(g)} \rightarrow 4C_{(s)} + D_{(l)}$. ΔH and ΔU are related as ……… **[Orissa JEE 2004]**

(a) $\Delta H = \Delta U$ (b) $\Delta H = \Delta U + 3RT$

(c) $\Delta H = \Delta U + RT$ (d) $\Delta H = \Delta U - 3RT$

IInd & IIIrd Law of thermodynamics and Entropy

1. For a reversible spontaneous change ΔS is

(a) $\frac{\Delta E}{T}$ (b) $\frac{P\,\Delta V}{T}$

(c) $\frac{q}{T}$ (d) *RT* log *K*

2. When disorder of a system increases, the change is said to be

(a) Exothermic (b) Non-spontaneous

(c) Endothermic (d) Spontaneous

3. The spontaneous flow of heat is always

(a) From low to high pressure

(b) From high to high pressure

(c) Unidirectional from lower temperature to higher temperature

(d) Unidirectional from the higher to lower temperature

4. Mixing of non-reacting gases is generally accompanied by

(a) Decrease in entropy

(b) Increase in entropy

(c) Change in enthalpy

(d) Change in free energy

5. An irreversible process occuring isothermally in an isolated system leads to

(a) Zero entropy

(b) An increase in the total entropy of the system

(c) A decrease in the total entropy of the system

(d) None of these

6. The entropy values (in JK^{-1} mol^{-1}) of $H_{2(g)}$ = 130.6, $Cl_{2(g)}$ = 223.0 and $HCl_{(g)}$ = 186.7 at 298 *K* and 1 *atm* pressure. Then entropy change for the reaction

$H_{2(g)} + Cl_{2(g)} \rightarrow 2HCl_{(g)}$ is

[BHU 2005]

(a) + 540.3 (b) + 727.3

(c) – 166.9 (d) + 19.8

7. Which of the following is the least random state of water

(a) Ice

(b) Liquid water

(c) Steam

(d) All present same random state

8. Which one of the following process is non-spontaneous

(a) Dissolution of $CuSO_4$ in water

(b) Reaction between H_2 and O_2 to form water

(c) Water flowing down hill

(d) Flow of electric current from low potential to high potential

9. Which of the following is zero during adiabatic expansion of the gas

(a) ΔT (b) ΔS

(c) ΔE (d) None of these

10. The entropy of crystalline substances at absolute zero going by the third law of thermodynamics should be taken as

[J & K 2005]

(a) 100

(b) 50

(c) Zero

(d) Different for different substances

11. In which state, the matter have highest entropy

(a) Solid (b) Liquid

(c) Gas (d) Equal in all

12. Which of the following pairs of a chemical reaction is certain to result in spontaneous reaction ? **[CBSE PMT 2005]**

(a) Exothermic and decreasing disorder

(b) Endothermic and increasing disorder

(c) Exothermic and increasing disorder

(d) Endothermic and decreasing disorder

13. When one mole of monoatomic ideal gas at T *K* undergoes adiabatic change under a constant external pressure of 1 atm changes volume from 1 litre to 2 litre.

The final temperature in Kelvin would be **[IIT 2005]**

(a) $\frac{T}{2^{(2/3)}}$ (b) $T+\frac{2}{3\times 0.0821}$

(c) T (d) $T-\frac{2}{3\times 0.0821}$

14. 9.0 *gm* of H_2O is vaporised at $100^{o}C$ and 1 *atm* pressure. If the latent heat of vaporisation of water is $x\,J\,/gm$, then ΔS is given by

(a) $\frac{x}{373}$ (b) $\frac{18x}{100}$

(c) $\frac{18x}{373}$ (d) $\frac{1}{2}\times\frac{18x}{373}$

15. The ΔS for the vaporisation of 1 mol of water is 88.3 *J/mole K*. The value of ΔS for the condensation of 1 *mol* of vapour will be

(a) 88.3 *J/mol K* (b) $(88.3)^2$ *J/mol K*

(c) – 88.3 *J/mol K* (d) $\frac{1}{88.3}$ *J/mol K*

16. For which reaction from the following, ΔS will be maximum

[AIIMS 1982, 83, 94; AMU 2000]

(a) $Ca(s)+\frac{1}{2}O_2(g)\rightarrow CaO(s)$

(b) $CaCO_3(s)\rightarrow CaO(s)+CO_2(g)$

(c) $C(s)+O_2(g)\rightarrow CO_2(g)$

(d) $N_2(g)+O_2(g)\rightarrow 2NO(g)$

17. The occurrence of a reaction is impossible if

[AIIMS 1982, 91; MP PET 1997;
MP PMT 1999; DPMT 2002]

(a) ΔH is +ve ; ΔS is also + ve but $\Delta H < T\Delta S$

(b) ΔH is – ve ; ΔS is also – ve but $\Delta H > T\Delta S$

(c) ΔH is – ve ; ΔS is + ve

(d) ΔH is + ve ; ΔS is – ve

18. If the enthalpy of vaporization for water is 186.5 *kJ* mol^{-1}, the entropy of its vaporization will be **[CPMT 1988; DCE 2000]**

(a) $0.5 JK^{-1} mol^{-1}$ (b) $1.0 JK^{-1} mol^{-1}$

(c) $1.5 JK^{-1} mol^{-1}$ (d) $2.0 JK^{-1} mol^{-1}$

19. Which of the following statement is true. The entropy of the universe **[MP PMT 1993; CET Pune 1998]**

(a) Increases and tends towards maximum value

(b) Decreases and tends to be zero

(c) Remains constant

(d) Decreases and increases with a periodic rate

20. When enthalpy and entropy change for a chemical reaction are $-2.5 \times 10^{3}\ cal$ and $7.4\ cal\ deg^{-1}$ respectively. Predict the reaction at $298\ K$ is **[AFMC 1998; MH CET 1999; CBSE PMT 2000]**

(a) Spontaneous (b) Reversible

(c) Irreversible (d) Non-spontaneous

21. The total entropy change for a system and its surroundings increases, if the process is

(a) Reversible (b) Irreversible

(c) Exothermic (d) Endothermic

22. For chemical reactions, the calculation of change in entropy is normally done

(a) At constant pressure

(b) At constant temperature

(c) At constant temperature and pressure both

(d) At constant volume

23. When the value of entropy is greater, then the ability of work

(a) Is maximum (b) Is minimum

(c) Is medium (d) None of these

24. Which of the following is true for the reaction $H_2O(l) \rightleftharpoons H_2O(g)$ at $100^{\circ} C$ and 1 atmosphere **[KCET 1991; AIIMS 1996]**

(a) $\Delta E = 0$ (b) $\Delta H = 0$

(c) $\Delta H = \Delta E$ (d) $\Delta H = T\Delta S$

25. The enthalpy change for the transition of liquid water to steam, $\Delta H_{vap} = 37.3 kJ\ mol^{-1}$ at $373 K$. The entropy change for the process is **[MP PET 1994]**

(a) $111.9 J\ mol^{-1} K^{-1}$ (b) $37.3 J\ mol^{-1} K^{-1}$

(c) $100 J\ mol^{-1} K^{-1}$ (d) $74.6 J\ mol^{-1} K^{-1}$

26. When a solid is converted into liquid, entropy **[MP PET 1993, 95; MP PMT 1996]**

(a) Becomes zero (b) Remains the same

(c) Decreases (d) Increases

27. In a spontaneous process, the entropy of the system and its surroundings **[MP PET 1996; NCERT 1975]**

(a) Equals zero (b) Decreases

(c) Increases (d) Remains constant

28. The positive value of ΔS indicates that **[MP PMT 1997]**

(a) The system becomes less disordered

(b) The system becomes more disordered

(c) The system is in equilibrium position

(d) The system tends to reach at equilibrium position

29. For reaction $2Cl(s) \rightarrow Cl_2(s)$, the signs of ΔH and ΔS respectively are **[KCET 1996]**

(a) +, – (b) +, +

(c) –, – (d) –, +

30. The enthalpy of water is $386 kJ$. What is entropy of water **[BHU 1997]**

(a) 0.5 *kJ* (b) 1.03 *kJ*

(c) 1.5 *kJ* (d) 22.05 *kJ*

31. For which of the processes is ΔS negative **[Pb. PMT 1998]**

(a) $H_2(g) \rightarrow 2H(g)$

(b) $N_2(g) 1 atm \rightarrow N_2(g) 8\ atm$

(c) $2SO_3(g) \rightarrow 2SO_2(g) + O_2(g)$

(d) $C_{(diamond)} \rightarrow C_{(graphite)}$

32. Identify the correct statement regarding entropy **[CBSE PMT 1998; BHU 2001]**

(a) At $0^{\circ} C$, the entropy of a perfectly crystalline substance is taken to be zero

(b) At absolute zero of temperature, the entropy of a perfectly crystalline substance is $+ve$

(c) At absolute zero of temperature, the entropy of all crystalline substances is taken to be zero

(d) At absolute zero of temperature, the entropy of a perfectly crystalline substance is taken to be zero

33. One mole of an ideal gas at $300K$ is expanded isothermally from an initial volume of 1 litre to 10 litres. The change in energy for this process is $(R = 2 cal mol^{-1} K^{-1})$ **[CBSE PMT 1998]**

(a) 163.7 *cal* (b) 850.2 *cal*

(c) 1381.1 *cal* (d) Zero

34. If $900 J / g$ of heat is exchanged at boiling point of water, then what is increase in entropy **[BHU 1998]**

(a) 43.4 *J/mole* (b) 87.2 *J/mole*

(c) 900 *J/mole* (d) Zero

35. A container has hydrogen and oxygen mixture in ratio of 4 : 1 by weight, then **[BHU 1998]**

(a) Internal energy of the mixture decreases

(b) Internal energy of the mixture increases

(c) Entropy of the mixture increases

(d) Entropy of the mixture decreases

36. If 0.75 *mole* of an ideal gas expands isothermally at $27^o C$ from 15 *litres* to 25 *litres,* the maximum work obtained is

[AFMC 1999]

(a) 8.40 *J*

(b) 9.34 *J*

(c) 10.86 *J*

(d) 10.43 *J*

37. In which of the following conditions a chemical reaction can not occur **[AMU 1999]**

(a) ΔH and ΔS increase and $T\Delta S > \Delta H$

(b) ΔH and ΔS decrease and $\Delta H > T\Delta S$

(c) ΔH increases and ΔS decreases

(d) ΔH decreases and ΔS increases

38. An engine operating between $150^o C$ and $25^o C$ takes 500 *J* heat from a higher temperature reservoir if there are no frictional losses, then work done by engine is

[MH CET 1999]

(a) 147.7 *J*

(b) 157.75 *J*

(c) 165.85 *J*

(d) 169.95 *J*

39. The entropy of a perfectly crystalline solid at absolute zero is

[AMU 2000]

(a) Positive

(b) Negative

(c) Zero

(d) Not definite

40. Which of the following conditions will always lead to a non-spontaneous change **[AMU 2000; KCET (Med.) 2000]**

(a) Positive ΔH and positive ΔS

(b) Negative ΔH and negative ΔS

(c) Positive ΔH and negative ΔS

(d) Negative ΔH and positive ΔS

41. Following data is known about melting of a compound *AB*. $\Delta H = 9.2 kJ\ mol^{-1}$, $\Delta S = 0.008 kJ\ K^{-1} mol^{-1}$. Its melting point is **[Pb. PMT 2000; AIIMS 2000]**

(a) 736 *K*

(b) 1050 *K*

(c) $1150 K$

(d) $1150^o C$

42. The volume of a gas decreases from $500 cc$ to $300 cc$ when a sample of gas is compressed by an average pressure of 0.6 *atm*. During this process 10 *J* of heat is liberated. The change in internal energy is **[Pb. PMT 2000]**

(a) – 2.16 *J*

(b) 12.156 *J*

(c) 2.16 *J*

(d) 101.3 *J*

43. The standard entropies of $CO_2(g), C(s)$ and $O_2(g)$ are 213.5, 5.690 and $205 JK^{-1}$ respectively. The standard entropy of formation of $CO_2(g)$ is **[CPMT 2001]**

(a) $1.86 JK^{-1}$

(b) $1.96 JK^{-1}$

(c) $2.81 JK^{-1}$

(d) $2.86 JK^{-1}$

44. Which of the following endothermic processes are spontaneous **[CBSE PMT 2001]**

(a) Melting of ice

(b) Evaporation of water

(c) Heat of combustion

(d) Both (a) and (b)

45. For the reaction $H_2O(s) \rightleftharpoons H_2O(l)$ at $0^o C$ and normal pressure **[KCET 2001]**

(a) $\Delta H > T\Delta S$

(b) $\Delta H = T\Delta S$

(c) $\Delta H = \Delta G$

(d) $\Delta H < T\Delta S$

46. One mole of an ideal gas is allowed to expand reversibly and adiabatically from a temperature of $27^o C$. If the work done during the process is 3 *kJ*, the final temperature will be equal to $(C_v = 20 JK^{-1})$

[KCET 2000; AFMC 2000; AIIMS 2001]

(a) 150 *K*

(b) 100 *K*

(c) $26.85^o C$

(d) 295 *K*

47. The entropy change, in the conversion of one mole of liquid water at 373 *K* to vapour at the same temperature is (Latent heat of vaporization of water, $\Delta H_{vap} = 2.257 kJ\ /g)$

[AFMC 2002; KCET 2002]

(a) 105.9 Jk^{-1}

(b) $107.9\ Jk^{-1}$

(c) $108.9\ Jk^{-1}$

(d) $109.9\ Jk^{-1}$

48. A heat engine absorbs heat Q_1 at temperature T_1 and heat Q_2 at temperature T_2. Work done by the engine is $(Q_1 + Q_2)$. This data **[AIEEE 2002]**

(a) Violates Ist law of thermodynamics

(b) Violates Ist law of thermodynamics if Q_1 is *–ve*

(c) Violates Ist law of thermodynamics if Q_2 is *–ve*

(d) Does not violate Ist law of thermodynamics

49. Equal volumes of monoatomic and diatomic gases at same initial temperature and pressure are mixed. The ratio of specific heats of the mixture (C_p / C_v) will be

[AFMC 2002]

(a) 1

(b) 2

(c) 1.67

(d) 1.5

50. The law formulated by Dr. Nernst is **[Kerala (Med.) 2002]**

(a) First law of thermodynamics

(b) Second law of thermodynamics

(c) Third law of thermodynamics

(d) Both (a) and (b)

51. The unit of entropy is **[CBSE PMT 2002]**

(a) $J\ mol^{-1}$ (b) $JK\ mol^{-1}$

(c) $J\ mol^{-1}K^{-1}$ (d) $J^{-1}K^{-1}mol^{1}$

52. The entropy changed involved in the conversion of 1 *mole* of liquid water at 373 *K* to vapour at the same temperature will be

$[\Delta H_{vap} = 2.257 kJ\ /\ gm]$ **[MP PET 2002]**

(a) 0.119 *kJ* (b) 0.109 *kJ*

(c) 0.129 *kJ* (d) 0.120 *kJ*

53. When a liquid boils, there is **[JIPMER 2002]**

(a) An increase in entropy

(b) A decrease in entropy

(c) An increase in heat of vaporization

(d) An increase in free energy

54. Which one of the following has ΔS^0 greater than zero **[AIIMS 2003]**

(a) $CaO + CO_2(g) \rightleftharpoons CaCO_3(s)$

(b) $NaCl(aq) \rightleftharpoons NaCl(s)$

(c) $NaNO_3(s) \rightleftharpoons Na^+(aq) + NO_3^-(aq)$

(d) $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$

55. The molar heat capacity of water at constant pressure is $75\ JK^{-1}mol^{-1}$. When 1.0 *kJ* of heat is supplied to 100 *g* of water which is free to expand the increase in temperature of water is **[CBSE PMT 2003]**

(a) 6.6 *K* (b) 1.2 *K*

(c) 2.4 *K* (d) 4.8 *K*

56. The work done to contract a gas in a cylinder, is 462 *joules*. 128 *joule* energy is evolved in the process. What will be the internal energy change in the process **[MP PMT 2003]**

(a) + 590 *joules* (b) – 334 *joules*

(c) + 334 *joules* (d) – 590 *joules*

57. Highest entropy is in **[BVP 2003]**

(a) Hydrogen (b) Water

(c) Graphite (d) Mercury

58. $\underset{S^0(298\,K)\,K^{-1}mol^{-1}}{H^+(aq)} + \underset{-10.7}{OH^-(aq)} \longrightarrow \underset{+70}{H_2O(l)}$

Standard entropy change for the above reaction is **[DPMT 2004]**

(a) $60.3\,JK^{-1}mol^{-1}$ (b) $80.7\,JK^{-1}mol^{-1}$

(c) $-70\,JK^{-1}mol^{-1}$ (d) $+10.7\,JK^{-1}mol^{-1}$

59. One mole of water at $100^o C$ is converted into steam at $100^o C$ at a constant pressure of 1 atm. The change in entropy is [heat of vaporisation of water at $100^o C = 540\,cal\,/\,gm$] **[Pb. PMT 2004]**

(a) 8.74 (b) 18.76

(c) 24.06 (d) 26.06

60. For a carnot engine, the source is at $500K$ and the sink at $300K$. What is efficiency of this engine **[BHU 2004]**

(a) 0.2 (b) 0.4

(c) 0.6 (d) 0.3

61. Heat require to raise the temperature of 1 mol of a substance by $1^o C$ is called **[DCE 2002]**

(a) Specific heat (b) Molar heat capacity

(c) Water equivalent (d) Specific gravity

62. Maximum entropy will be in which of the following **[DCE 2004]**

(a) Ice (b) Liquid water

(c) Snow (d) Water vapours

63. The standard entropies of $CO_2(g), C(s)$ and $O_2(g)$ are 213.5, 5.740 and 205 JK^{-1} respectively. The standard entropy of formation of CO_2 is **[Pb. CET 2001]**

(a) $2.76\,JK^{-1}$ (b) $2.12\,JK^{-1}$

(c) $1.12\,JK^{-1}$ (d) $1.40\,JK^{-1}$

64. Which law of thermodyanamics help in calculating entropy at different temperatures **[Pb. CET 2003]**

(a) First law (b) Second law

(c) Third law (d) Zeroth law

65. Entropy is maximum in case of **[BVP 2004]**

(a) Steam (b) Water at $0^o C$

(c) Water at $4^o C$ (d) Ice

66. Considering entropy (S) as a thermodynamic parameter, the criterion for the spontaneity of any process is **[CBSE PMT 2004]**

(a) $\Delta S_{system} > 0$ only

(b) $\Delta S_{surroundings} > 0$ only

(c) $\Delta S_{system} + \Delta S_{surroundings} > 0$

(d) $\Delta S_{system} - \Delta S_{surroundings} > 0$

67. A process is taking place at constant temperature and pressure. Then **[KCET 2004]**

(a) $\Delta H = \Delta E$ (b) $\Delta H = T\Delta S$

(c) $\Delta H = 0$ (d) $\Delta S = 0$

68. The enthalpy of vapourization of a liquid is $30\,kJ\ mol^{-1}$ and entropy of vapourization is $75\,J\ mol^{-1}K$. The boiling point of the liquid at 1 *atm* is **[IIT JEE (Screening) 2004]**

(a) 250*K* (b) 400*K*

(c) 450*K* (d) 600*K*

Heat of reaction

1. If $C+O_2 \rightarrow CO_2+94.2\,kcal$

$$H_2+\frac{1}{2}O_2 \rightarrow H_2O+68.3\,kcal$$

$$CH_4+2O_2 \rightarrow CO_2+2H_2O+210.8\,kcal$$

then the possible heat of methane will be **[MP PET 1990]**

(a) 47.3 *kcal* (b) 20.0 *kcal*

(c) 45.9 *kcal* (d) – 47.3 *kcal*

2. Molar heat of vaporisation of a liquid is $6kJ\ mol^{-1}$. If the entropy change is $16J\ mol^{-1}\ K^{-1}$, the boiling point of the liquid is **[KCET 2005]**

(a) $375^o C$ (b) $375K$

(c) $273K$ (d) $102^o C$

3. The enthalpy of fusion of ice per mole

(a) 18 *kJ* (b) 8 *kJ*

(c) 80 *kJ* (d) 6 *kJ*

4. In which of the following neutralisation reactions, the heat of neutralisation will be highest

[MP PMT 1989, 91; AIIMS 1999]

(a) NH_4OH and CH_3COOH

(b) NH_4OH and HCl

(c) $NaOH$ and CH_3COOH

(d) $NaOH$ and HCl

5. If $S+O_2 \rightarrow SO_2; (\Delta H=-298.2)$

$$SO_2+\frac{1}{2}O_2 \rightarrow SO_3; (\Delta H=-98.2)$$

$$SO_3+H_2O \rightarrow H_2SO_4; (\Delta H=-130.2)$$

$$H_2+\frac{1}{2}O_2 \rightarrow H_2O; (\Delta H=-287.3)$$

then the enthalpy of formation of H_2SO_4 at 298K will be

[DPMT 1983; Orissa JEE 2005]

(a) $-433.7\,kJ$ (b) $-650.3\,kJ$

(c) $+320.5\,kJ$ (d) $-813.9\,kJ$

6. From Kirchhoff's equation which factor affects the heat of reaction **[MP PMT 1990]**

(a) Pressure (b) Temperature

(c) Volume (d) Molecularity

7. The molar neutralization heat for KOH and HNO_3 as compared to molar neutralization heat of $NaOH$ and HCl

[MP PMT 1989]

(a) Less (b) More

(c) Equal (d) Depends on pressure

8. An exothermic reaction is one in which the reacting substances **[CPMT 1974, 79; Bihar MEE 1982; KCET 1992; JIPMER 2001]**

(a) Have more energy than the products

(b) Have less energy than the products

(c) Are at a higher temperature than the product

(d) None of the above

9. The heat evolved in the combustion of benzene is given by

$$C_6H_6+7\frac{1}{2}O_2 \rightarrow 6CO_2(g)+3H_2O(l); \Delta H=-3264.6\,kJ$$

Which of the following quantities of heat energy will be evolved when $39\,g\,C_6H_6$ are burnt

[NCERT 1978; MP PET 1990; JIPMER 2001]

(a) 816.15 *kJ* (b) 1632.3 *kJ*

(c) 6528.2 *kJ* (d) 2448.45 *kJ*

10. Thermochemical reactions

$$C(\text{graphite})+\frac{1}{2}O_2(g) \rightarrow CO(g); \Delta H=-110.5\,kJ$$

$$CO(g)+\frac{1}{2}O_2(g) \rightarrow CO_2(g); \Delta H=-283.2\,kJ$$

From the above reaction, the heat of reaction for $C(\text{graphite})+O_2(g) \rightarrow CO_2(g)$ will be

[CPMT 1988; MP PMT 1989]

(a) – 393.7 *kJ* (b) + 393.7 *kJ*

(c) – 172.7 *kJ* (d) + 172.7 *kJ*

11. The following is (are) endothermic reaction **[IIT JEE 1999]**

(a) Combustion of methane

(b) Decomposition of water

(c) Dehydrogenation of ethane to ethylene

(d) Conversion of graphite to diamond

12. Evaporation of water is

[CPMT 1973; DPMT 1982; MP PMT 1989; MP PET 1999]

(a) An endothermic change

(b) An exothermic change

(c) A process where no heat change occurs

(d) A process accompanied by chemical reaction

13. An exothermic reaction is one which

[NCERT 1977; MP PMT 1990]

(a) Takes place only on heating

(b) Is accompanied by a flame

(c) Is accompanied by a absorption of heat

(d) Is accompanied by evolution of heat

14. An endothermic reaction is one in which

[MNR 1980; NCERT 1976]

(a) Heat is converted into electricity

(b) Heat is absorbed
(c) Heat is evolved
(d) Heat is converted into mechanical work

15. Which of the following statement is correct **[NCERT 1978]**

(a) ΔH is positive for exothermic reaction
(b) ΔH is negative for endothermic reaction
(c) The heat of neutralization of strong acid and strong base is always the same
(d) The enthalpy of fusion is negative

16. The absolute enthalphy of neutralisation of the reaction $MgO(s)+2HCl(aq)\rightarrow MgCl_2(aq)+H_2O(l)$ will be **[CBSE PMT 2005]**

(a) Less than $-57.33\ kJ\ mol^{-1}$
(b) $-57.33\ kJ\ mol^{-1}$
(c) Greater than $-57.33\ kJ\ mol^{-1}$
(d) $57.33\ kJ\ mol^{-1}$

17. ΔH°_f (298 *K*) of methanol is given by the chemical equation **[AIIMS 2005]**

(a) $CH_4(g)+1/2O_2(g)\rightarrow CH_3OH(g)$
(b) C (graphite) $+1/2O_2(g)+2H_2(g)\rightarrow CH_3OH(l)$
(c) C (diamond) $+1/2O_2(g)+2H_2(g)\rightarrow CH_3OH(l)$
(d) $CO(g)+2H_2(g)\rightarrow CH_3OH(l)$

18. If ΔH_f^{o} for H_2O_2 and H_2O are $-188kJ/mole$ and $-286kJ/mole$. What will be the enthalpy change of the reaction $2H_2O_2(l)\rightarrow 2H_2O(l)+O_2(g)$ **[MP PMT 1992]**

(a) $-196kJ/mole$ (b) $146kJ/mole$
(c) $-494kJ/mole$ (d) $-98kJ/mole$

19. The heat of transition (ΔH_t) of graphite into diamond would be, where

$$C(\text{graphite})+O_2(g)\rightarrow CO_2(g);\ \Delta H=x\,kJ$$

$$C(\text{diamond})+C_2(g)\rightarrow CO_2(g);\ \Delta H=y\,kJ$$

[Pb. PET 1985]

(a) $(x+y)kJ\ mol^{-1}$ (b) $(x-y)kJ\ mol^{-1}$
(c) $(y-x)kJ\ mol^{-1}$ (d) None of these

20. Correct relationship between heat of fusion (ΔH_{fus}), heat of vaporization (ΔH_{vap}) and heat of sublimation (ΔH_{sub}) is

(a) $\Delta H_{fus}=\Delta H_{vap}+\Delta H_{sub}$
(b) $\Delta H_{vap}=\Delta H_{fus}+\Delta H_{sub}$
(c) $\Delta H_{sub}=\Delta H_{vap}+\Delta H_{fus}$
(d) $\Delta H_{sub}=\Delta H_{vap}-\Delta H_{fus}$

21. Which of the following is an example of endothermic reaction **[MP PMT 1980]**

(a) $C_2H_2+2H_2\rightarrow C_2H_6;\ \Delta E=-314.0kJ$
(b) $C+O_2\rightarrow CO_2;\ \Delta E=-393.5kJ$
(c) $N_2+O_2\rightarrow 2NO;\ \Delta E-180.5kJ$
(d) $2H_2+O_2\rightarrow 2H_2O;\ \Delta E+571.8kJ$

22. If the enthalpy of B is greater than of *A*, the reaction $A\rightarrow B$ is **[MP PMT 1997]**

(a) Endothermic (b) Exothermic
(c) Instantaneous (d) Spontaneous

23. Given that

$$2C(s)+2O_2(g)\rightarrow 2CO_2(g);\ \Delta H=-787kJ$$

$$H_2(g)+\frac{1}{2}O_2(g)\rightarrow H_2O(l);\ \Delta H=-286kJ$$

$$C_2H_2(g)+2\frac{1}{2}O_2(g)\rightarrow 2CO_2(g)+H_2O(l);\Delta H=-1301kJ$$

Heat of formation of acetylene is **[KCET 1989; Orissa JEE 2005]**

(a) $-1802kJ$ (b) $+1802kJ$
(c) $-800kJ$ (d) $+228kJ$

24. Enthalpy change for reaction, $\frac{1}{2}H_2+\frac{1}{2}Cl_2\rightarrow HCl$, is called

(a) Enthalpy of combination (b) Enthalpy of reaction
(c) Enthalpy of formation (d) Enthalpy of fusion

25. The enthalpy of neutralization is about 57.3 *kJ* for the pair

(a) HCl and NH_4OH
(b) NH_4OH and HNO_3
(c) HCl and $NaOH$
(d) CH_3COOH and $NaOH$

26. Conversion of oxygen to ozone represented by the equation $3O_2\rightarrow 2O_3$ is an endothermic reaction. Enthalpy change ΔH accompanying the reaction **[KCET 1988, 92]**

(a) Is negative (b) Is positive
(c) Is zero (d) Depends on temperature

27. The mutual heat of neutralisation of 40 *gm* of $NaOH$ and 60 *gm* CH_3COOH will be **[MP PET/PMT 1988]**

(a) 56.1 *kcal* (b) Less than 56.1 *kcal*
(c) More than 56.1 *kcal* (d) 13.7 *kcal*

28. The heat of formations of $CO(g)$ and $CO_2(g)$ are -26.4 *kcal* and -94.0 *kcal* respectively. The heat of combustion of carbon monoxide will be

[MP PET/PMT 1988; EAMCET 1993]

(a) $+26.4\,kcal$ (b) $-67.6\,kcal$

(c) $-120.6\,kcal$ (d) $+52.8\,kcal$

29. The enthalpy of combustion at 25°C of H_2, cyclohexane (C_6H_{12}) and cyclohexene (C_6H_{10}) are –241, –3920 and –800 *KJ / mole* respectively. The heat of hydrogenation of cyclohexene is **[BHU 2005]**

(a) – 121 *KJ / mole* (b) + 121 *KJ / mole*

(c) – 242 *KJ / mole* (d) + 242 *KJ / mole*

30. Heat of neutralisation of NH_4OH and HCl is

[EAMCET 1980; Roorkee 1990; MP PMT 1994]

(a) $13.7\,kcal$ (b) $>13.7\,kcal$

(c) $<13.7\,kcal$ (d) None of the above

31. Heat of combustion ΔH of CH_4, C_2H_6, C_2H_4 and C_2H_2 gases are – 212.8, – 373.0, – 337.0 and – 310.5 *kcal* respectively at the same temperature. The best fuel among these gases is

(a) CH_4 (b) C_2H_6

(c) C_2H_4 (d) C_2H_2

32. Heat of formation of $CO_2(g)$, $H_2O(l)$ and $CH_4(g)$ are – 94.0, – 68.4 and – 17.9 *kcal* respectively. The heat of combustion of methane is

(a) – 212.9 *kcal* (b) – 136.8 *kcal*

(c) – 304.3 *kcal* (d) – 105.2 *kcal*

33. The heat of reaction does not depend upon

(a) Temperature of the reaction

(b) Physical state of reactants and products

(c) Whether the reaction is carried out at constant pressure or at constant volume

(d) The method by which the final products are obtained from the reactants

34. Heat of neutralisation of a strong acid by a strong base is a constant value because **[KCET 1984]**

(a) Salt formed does not hydrolyse

(b) Only H^+ and OH^- ions react in every case

(c) The strong base and strong acid react completely

(d) The strong base and strong acid react in aqueous solution

35. Heat of neutralisation of an acid by a base is highest when

[KCET 1985]

(a) Both the acid and base are weak

(b) Both the acid and base are strong

(c) The acid is strong and the base is weak

(d) The acid is weak and the base is strong

36. The standard molar heat of formation of ethane, CO_2 and water (l) are respectively – 21.1, – 94.1 and – 68.3 *kcal*. The standard molar heat of combustion of ethane will be

[IIT JEE 1986; DPMT 2005]

(a) – 372 *kcal* (b) 162 *kcal*

(c) –240 *kcal* (d) 183.5 *kcal*

37. Which of the following reaction is endothermic

[AFMC 1988]

(a) $CaCO_3 \rightarrow CaO + CO_2$

(b) $Fe + S \rightarrow FeS$

(c) $NaOH + HCl \rightarrow NaCl + H_2O$

(d) $CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$

38. In the reaction

$$CO_2(g) + H_2(g) \rightarrow CO(g) + H_2O(g); \Delta H = 80kJ$$

ΔH is known as

[CPMT 1987; KCET 1993; Bihar CEE 1995]

(a) Heat of formation (b) Heat of combustion

(c) Heat of neutralization (d) Heat of reaction

39. Heat of combustion of a substance

[CPMT 1987, 96; AFMC 1992]

(a) Is always positive

(b) Is always negative

(c) Is equal to heat of formation

(d) Nothing can be said without reaction

40. The heat change for the reaction $H_2 + \frac{1}{2}O_2 \rightarrow H_2O$ is called

(a) Heat of reaction (b) Heat of formation

(c) Heat of vaporisation (d) None of the above

41. The heat change ΔH for the reaction $2CO + O_2 \rightarrow 2CO_2; \Delta H = -135kcal$ is called

(a) Heat of formation (b) Heat of reaction

(c) Heat of combustion (d) Heat of solution

42. The heats of combustion of rhombic and monoclinic sulphur are respectively 70960 and 71030 calories. What will be the heat of conversion of rhombic sulphur to monoclinic

[MP PMT/PET 1988]

(a) 70960 calories (b) 71030 calories

(c) – 70 calories (d) + 70 calories

43. The heat of formation of $H_2O(l)$ is – 68.0 *kcal*, the heat of formation of $H_2O(g)$ is likely to be

(a) – 68.0 *kcal* (b) – 67.4 *kcal*

(c) 80.0 *kcal* (d) – 58.3 *kcal*

44. Which of the following fuels will have the highest calorific value (*kJ/kg*) **[MP PMT 1990]**

(a) Charcoal (b) Kerosene

(c) Wood (d) Dung

45. The heat of combustion of carbon is –94 *kcal* at 1 *atm* pressure. The intrinsic energy of CO_2 is

(a) $+94 kcal$ (b) $-94 kcal$

(c) $+47 kcal$ (d) $-47 kcal$

46. The heat of neutralisation of a strong acid and a strong alkali is $57.0 kJ\ mol^{-1}$. The heat released when $0.5 mole$ of HNO_3 solution is mixed with $0.2 mole$ of KOH is

[KCET 1991; AIIMS 2002; AMU (Engg.) 2002]

(a) $57.0 kJ$ (b) $11.4 kJ$

(c) $28.5 kJ$ (d) $34.9 kJ$

47. A solution of $500 ml$ of $0.2 M\ KOH$ and $500 ml$ of $0.2 M\ HCl$ is mixed and stirred; the rise in temperature is T_1. The experiment is repeated using $250 ml$ each of solution, the temperature raised is T_2. Which of the following is true **[EAMCET 1987; MP PET 1994]**

(a) $T_1 = T_2$ (b) $T_1 = 2T_2$

(c) $T_1 = 4T_2$ (d) $T_2 = 9T_1$

48. Enthalpy of a compound is equal to its

[CMC Vellore 1991]

(a) Heat of combustion (b) Heat of formation

(c) Heat of reaction (d) Heat of solution

(e) Heat of dilution

49. Which is the best definition of "heat of neutralization"

[CMC Vellore 1991]

(a) The heat set free when one gram molecule of a base is neutralized by one gram molecule of an acid in dilute solution at a stated temperature

(b) The heat absorbed when one gram molecule of an acid is neutralized by one gram molecule of a base in dilute solution at a stated temperature

(c) The heat set free or absorbed when one gram atom of an acid is neutralized by one gram atom of a base at a stated temperature

(d) The heat set free or absorbed when a normal solution containing one gram equivalent of an acid is neutralized by a normal solution containing one gram equivalent of a base at a stated temperature

(e) The heat set free when one gram equivalent of an acid is neutralized by one gram equivalent of a base in dilute solution at a stated temperature

50. The compound with negative heat of formation are known as **[DPMT 1981]**

(a) Endothermic compound

(b) Exothermic compound

(c) Heat of formation compound

(d) None of the above

51. If $H^+ + OH^- \rightarrow H_2O + 13.7 kcal$, then the heat of neutralization for complete neutralization of one mole of H_2SO_4 by base will be **[MP PMT 1990]**

(a) 13.7 *kcal* (b) 27.4 *kcal*

(c) 6.85 *kcal* (d) 3.425 *kcal*

52. The lowest value of heat of neutralization is obtained for

[KCET 1988; MP PMT 1990]

(a) $HCl + NaOH$

(b) $CH_3COOH + NH_4OH$

(c) $NH_4OH + HCl$

(d) $NaOH + CH_3COOH$

53. Heat of neutralisation for the given reaction $NaOH + HCl \rightarrow NaCl + H_2O$ is $57.1 kJ\ mol^{-1}$. What will be the heat released when $0.25 mole$ of $NaOH$ is titrated against $0.25 mole$ of HCl **[CPMT 1990]**

(a) $22.5 kJ\ mol^{-1}$ (b) $57.1 kJ\ mol^{-1}$

(c) $14.3 kJ\ mol^{-1}$ (d) $28.6 kJ\ mol^{-1}$

54. Reaction, $H_2(g) + I_2(g) \rightarrow 2HI(g)$ $\Delta H = -12.40 kcal$. According to this, the heat of formation of *HI* will be

[MP PET 1990]

(a) 12.4 *kcal* (b) – 12.4 *kcal*

(c) – 6.20 *kcal* (d) 6.20 *kcal*

55. All reactions with chemical dissociation are **[MP PMT 1990]**

(a) Reversible

(b) Reversible and endothermic

(c) Exothermic

(d) Reversible or irriversible and endothermic or exothermic

56. The heat of formation is the change in enthalpy accompanying the formation of a substance from its elements at 298 *K* and 1 atm pressure. Since the enthalpies of elements are taken to be zero, the heat of formation (ΔH) of compounds **[NCERT 1978; KCET 1993]**

(a) Is always negative

(b) Is always positive

(c) May be negative or positive

(d) Is zero

57. The heat of combustion of $CH_{4(g)}, C_{(graphite)}$ and $H_{2(g)}$ are $20 kcal, -40 kcal$ and $-10 kcal$ respectively. The heat of formation of methane is **[EAMCET 1998]**

(a) $-4.0 kcal$ (b) $+40 kcal$

(c) $-80 kcal$ (d) $+80 kcal$

58. If a chemical reaction is accompanied by the evolution of heat, it is **[BHU 1979]**

(a) Catalytic (b) Photochemical

(c) Endothermic (d) Exothermic

59. A reaction that takes place with the absorption of energy is

[EAMCET 1977]

(a) Burning of a candle (b) Rusting of iron

(c) Electrolysis of water (d) Digestion of food

60. Which of the following is an endothermic reaction **[EAMCET 1980; MP PMT 1980; IIT JEE 1989; JIPMER 2002]**

(a) $2H_2 + O_2 \rightarrow 2H_2O$

(b) $N_2 + O_2 \rightarrow 2NO$

(c) $2NaOH + H_2SO_4 \rightarrow Na_2SO_4 + 2H_2O$

(d) $3O_2 + C_2H_5OH \rightarrow 2CO_2 + 3H_2O$

61. One of the phenomena which cannot be described as combustion is **[EAMCET 1979]**

(a) Oxidation of coal in air

(b) Burning of magnesium in nitrogen

(c) Reaction of antimony in chlorine

(d) Lighting of an electric lamp

62. Which of the following statements is correct about heat of combustion **[MADT Bihar 1982]**

(a) It may be exothermic in some cases and endothermic in other cases

(b) It is applicable to gaseous substances only

(c) It is always an exothermic reaction

(d) Its value does not change with temperature

63. $H_2 + \frac{1}{2}O_2 \rightarrow H_2O; \Delta H = -68.39 kcal$

$K + H_2O +$ Water

$\rightarrow KOH\ (aq) + \frac{1}{2}H_2; \Delta H = -48 kcal$

$KOH +$ Water $\rightarrow KOH\ (aq); \Delta H = -14 kcal$

The heat of formation of KOH is (in *kcal*) **[CPMT 1988]**

(a) $-68.39 + 48 - 14$ (b) $-68.39 - 48 + 14$

(c) $68.39 - 48 + 14$ (d) 68.39 + 48 + 14

64. Which of the following reaction can be used to define the heat of formation of $CO_2(g)$

[MP PMT 1989; MH CET 2001]

(a) $C(\text{graphite}) + O_2(g) = CO_2(g)$

(b) $CH_4(g) + 2O_2(g) = CO_2(g) + 2H_2O(l)$

(c) $CO(g) + \frac{1}{2}O_2(g) = CO_2(g)$

(d) $C_6H_6(l) + 7\frac{1}{2}O_2(g) = 6CO_2 + 3H_2O(l)$

65. The enthalpy of formation of ammonia is $-46.0 kJ\ mol^{-1}$. The enthalpy change for the reaction $2NH_3(g) \rightarrow 2N_2(g) + 3H_2(g)$ is

(a) 46.0 *kJ* mol^{-1} (b) 92.0 *kJ* mol^{-1}

(c) – 23.0 *kJ* mol^{-1} (d) – 92.0 *kJ* mol^{-1}

66. The heat of combustion of benzene determined in a bomb calorimeter is $-870 kcal mol^{-1}$ at $25^0 C$. The value of ΔE for the reaction is

(a) $-1740 kcal$ (b) $-870 kcal$

(c) $-872 kcal$ (d) $-874 kcal$

67. The formation of water from $H_2(g)$ and $O_2(g)$ is an exothermic reaction because **[MP PMT/PET 1988]**

(a) The chemical energy of $H_2(g)$ and $O_2(g)$ is more than that of water

(b) The chemical energy of $H_2(g)$ and $O_2(g)$ is less than that of water

(c) Not dependent on energy

(d) The temperature of $H_2(g)$ and $O_2(g)$ is more than that of water

68. In the reaction for the transition of carbon in the diamond form to carbon in the graphite form, ΔH is $-453.5 cal$. This points out that **[BHU 1981; KCET 1986, 89]**

(a) Graphite is chemically different from diamond

(b) Graphite is as stable as diamond

(c) Graphite is more stable than diamond

(d) Diamond is more stable than graphite

69. In the combustion of hydrocarbons, ΔH is **[BHU 1981]**

(a) Negative (b) Zero

(c) Positive (d) Undeterminate

70. The standard heats of formation in *kcal* mol^{-1} of $NO_2(g)$ and $N_2O_4(g)$ are 8.0 and 2.0 respectively. The heat of dimerization of NO_2 in $kcal$ is

$2NO_2(g) = N_2O_4(g)$ **[NCERT 1983]**

(a) 10.0 (b) – 6.0

(c) – 12.0 (d) – 14.0

71. The difference between heats of reaction at constant pressure and at constant volume for the reaction $2C_6H_6(l) + 15O_2(g) \rightarrow 12CO_2(g) + 6H_2O(l)$ at 25^0C in *kJ* is

[IIT JEE 1991; Kerala PMT 2004]

(a) –7.43 (b) + 3.72

(c) –3.72 (d) + 7.43

72. C (diamond) $+ C_2(g) \rightarrow CO_2(g); \Delta H = -395\ kJ$

C (graphite) $+ O_2(g) \rightarrow CO_2(g); \Delta H = -393.5\ kJ$

From the data, the ΔH when diamond is formed from graphite, is **[CBSE PMT 1989; BHU 1987]**

(a) $-1.5\,kJ$ (b) $+1.5\,kJ$

(c) $+3.0\,kJ$ (d) $-3.0\,kJ$

73. Which of the following values of heat of formation indicates that the product is least stable **[MP PMT 1991]**

(a) $-94\,kcal$ (b) $-231.6\,kcal$

(c) $+21.4\,kcal$ (d) $+64.8\,kcal$

74. Which of the following equations correctly represents the standard heat of formation (ΔH_f^o) of methane

[IIT JEE (Screening) 1992]

(a) $C(diamond) + 2H_2(g) = CH_4(g)$

(b) $C(graphite) + 2H_2(g) = CH_4(l)$

(c) $C(graphite) + 2H_2(g) = CH_4(g)$

(d) $C(graphite) + 4H = CH_4(g)$

75. In which of the following reactions does the heat change represent the heat of formation of water **[EAMCET 1991]**

(a)

$2H_2(g) + O_2(g) \rightarrow 2H_2O(l); \Delta H = -116\,kcal$

(b)

$H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(l); \Delta H = -58\,kcal$

(c)

$H^+(aq.) + OH^-(aq.) \rightarrow 2H_2O(l); \Delta H = -13.7\,kcal$

(d) $C_2H_2(g) + 2\frac{1}{2}O_2(g) \rightarrow 2CO_2(g) + H_2O(l)$;

$\Delta H = -310\,kcal$

76. Values of heats of formation for SiO_2 and MgO are -48.4 and $-34.7\,kJ$ respectively. The heat of the reaction $2Mg + SiO_2 \rightarrow 2MgO + Si$ is **[KCET 1990]**

(a) $21.16\,kJ$ (b) $-21.10\,kJ$

(c) $-13.62\,kJ$ (d) $13.6\,kJ$

77. Based on the following thermochemical equations

$H_2O(g) + C(s) \rightarrow CO(g) + H_2(g); \Delta H = 131\,kJ$

$CO(g) + \frac{1}{2}O_2(g) \rightarrow CO_2(g); \Delta H = -282\,kJ$

$H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(g); \Delta H = -242\,kJ$

$C(s) + O_2(g) \rightarrow CO_2(g); \Delta H = X\ kJ$

The value of X is **[CBSE PMT 1992]**

(a) $-393\,kJ$ (b) $-655\,kJ$

(c) $+393\,kJ$ (d) $+655\,kJ$

78. Heat of transition is the heat evolved or absorbed when a substance is converted from **[KCET 1984]**

(a) Solid to liquid

(b) Solid to vapour

(c) Liquid to vapour

(d) One allotropic form to another allotropic form

79. For the allotropic change represented by equation $C(diamond) \rightarrow C(graphite)$; the enthalpy change is $\Delta H = -1.89\,kJ$. If $6\,g$ of diamond and $6\,g$ of graphite are separately burnt to yield carbon dioxide, the heat liberated in the first case is **[KCET 1988; DPMT 2000]**

(a) Less than in the second case by $1.89\,kJ$

(b) More than in the second case by $1.89\,kJ$

(c) Less than in the second case by $11.34\,kJ$

(d) More than in the second case by $0.945\,kJ$

80. For an exothermic reaction

[MP PET 1994; Manipal MEE 1995]

(a) H of the products is less than H of the reactants

(b) H of the products is more than H of the reactants

(c) H of the products is equal to H of the reactants

(d) ΔH is always positive

81. The energy evolved is highest for which of the following reactions **[MP PET 1994]**

(a) $F + e^- \rightarrow F^{-1}$ (b) $Cl + e^- \rightarrow Cl^-$

(c) $S + 2e^- \rightarrow S^{2-}$ (d) $O + 2e^- \rightarrow O^{2-}$

82. In the combustion of $2.0\,gm$ of methane $25\,kcal$ heat is liberated, heat of combustion of methane would be

[MP PMT 1994]

(a) $100\,kcal$ (b) $200\,kcal$

(c) $300\,kcal$ (d) $400\,kcal$

83. Complete combustion of CH_4 gives **[BHU 1995]**

(a) $CO_2 + H_2O$ (b) $CO_2 + H_2$

(c) $COCl_2$ (d) $CO + CO_2 + H_2O$

84. If enthalpies of formation of $C_2H_4(g), CO_2(g)$ and $H_2O(l)$ at 25^0C and $1 atm$ pressure be 52, – 394 and $-286 kJ\ mol^{-1}$ respectively, the enthalpy of combustion of $C_2H_4(g)$ will be

[CBSE PMT 1995; AIIMS 1998; Pb. PMT 1999]

(a) $+1412 kJ\ mol^{-1}$ (b) $-1412 kJ\ mol^{-1}$

(c) $+141.2 kJ\ mol^{-1}$ (d) $-141.2 kJ\ mol^{-1}$

85. Carbon and carbon monoxide burn in oxygen to form carbon dioxide according to the following reactions

$$C + O_2 \rightarrow CO_2; \Delta H = -394 kJ\ mol^{-1}$$

$$2CO + O_2 \rightarrow 2CO_2; \Delta H = -569 kJ\ mol^{-1}$$

The heat of formation of $1 mol$ of carbon monoxide is thus

[MP PET 1995]

(a) $-219.0 kJ\ mol^{-1}$ (b) $-109.5 kJ\ mol^{-1}$

(c) $-175.0 kJ\ mol^{-1}$ (d) $-87.5 kJ\ mol^{-1}$

86. Heat of formation in the reaction $H_2 + Cl_2 \rightarrow 2HCl + 44 kcal$ is **[MP PMT 1995]**

(a) 44 *kcal* (b) 44000 *kcal*

(c) 22 *kcal* (d) 11 *kcal*

87. When water is added to quick lime, the reaction is

[MP PMT 1995]

(a) Exothermic (b) Endothermic

(c) Explosive (d) None of these

88. In an exothermic reaction ΔH is

[MP PMT 1995; CPMT 1999]

(a) Positive (b) Negative

(c) Zero (d) Both positive or negative

89. The heat change for the following reaction $C(s) + 2S(s) \rightarrow CS_2(l)$ is known as **[MP PMT 1996]**

(a) Heat of vaporization (b) Heat of solution

(c) Heat of fusion (d) Heat of formation

90. The enthalpy of combustion of benzene from the following data will be

(i) $6C(s) + 3H_2(g) \rightarrow C_6H_6(l); \Delta H = +45.9 kJ$

(ii)

$$H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(l); \Delta H = -285.9 kJ$$

(iii) $C(s) + O_2(g) \rightarrow CO_2(g); \Delta H = -393.5 kJ$

(a) + 3172.8 *kJ* (b) – 1549.2 *kJ*

(c) – 3172.8 *kJ* (d) – 3264.6 *kJ*

91. Enthalpy of formation of HF and HCl are $-161 kJ$ and $-92 kJ$ respectively. Which of the following statements is incorrect **[KCET 2003]**

(a) HCl is more stable than HF

(b) HF and HCl are exothermic compounds

(c) The affinity of fluorine to hydrogen is greater than the affinity of chlorine to hydrogen

(d) HF is more stable than HCl

92. The heat of reaction at constant pressure is given by

[MP PMT 1997]

(a) $E_P - E_R$ (b) $E_R - E_P$

(c) $H_P - H_R$ (d) $H_R - H_P$

93. In an endothermic reaction, the value of ΔH is

[CBSE PMT 1999; AIIMS 1998; BHU 2000; MP PMT 2000]

(a) Zero (b) Positive

(c) Negative (d) Constant

94. $2.2016 gm$ of acetaldehyde produced $13.95 kcal$ of heat on combustion in O_2. Calculate the heat of combustion of CH_3CHO **[Bihar CEE 1995]**

(a) 279 *kcal* (b) 972 *kcal*

(c) 27.9 *kcal* (d) 2.79 *kcal*

95. $C + \frac{1}{2}O_2 \rightarrow CO; \Delta H = -42 kJ$

$$CO + \frac{1}{2}O_2 \rightarrow CO_2; \Delta H = -24 kJ$$

The heat of formation of CO_2 is

[CPMT 1996]

(a) – 16 *kJ* (b) + 66 *kJ*

(c) + 16 *kJ* (d) – 66 *kJ*

96. Standard molar enthalpy of formation of CO_2 is equal to

[IIT JEE 1997; BHU 2001]

(a) Zero

(b) The standard molar enthalpy of combustion of gaseous carbon

(c) The sum of standard molar enthalpies of formation of CO and O_2

(d) The standard molar enthalpy of combustion of carbon (graphite)

97. In the complete combustion of butanol $C_4H_9OH(l)$, if ΔH is enthalpy of combustion and ΔE is the heat of combustion at constant volume, then **[EAMCET 1997]**

(a) $\Delta H < \Delta E$

(b) $\Delta H = \Delta E$

(c) $\Delta H > \Delta E$

(d) $\Delta H, \Delta E$ relation cannot be predicted

98. $C + O_2 \to CO_2; \Delta H = X$

$CO + \frac{1}{2}O_2 \to CO_2; \Delta H = Y$

Then the heat of formation of CO is

[BHU 1997; DPMT 2002]

(a) $X - Y$ (b) $Y - 2X$

(c) $X + Y$ (d) $2X - Y$

99. The values of heat of formation of SO_2 and SO_3 are $-298.2 kJ$ and $-98.2 kJ$. The heat of reaction of the following reaction will be

$SO_2 + \frac{1}{2}O_2 \to SO_3$ **[BHU 1997; CBSE PMT 2000]**

(a) $-200 kJ$ (b) $-356.2 kJ$

(c) $+200 kJ$ (d) $-396.2 kJ$

100. Calculate the standard heat of formation of carbon disulphide (l), given that the standard heat of combustion of carbon (s), sulphur (s) and carbon disulphide (l) are $-393.3, -293.72$ and $-1108.76 kJ\ mol^{-1}$ respectively

[Roorkee 1989; BHU 1997]

(a) $-128.02 kJ\ mol^{-1}$ (b) $+12.802 kJ\ mol^{-1}$

(c) $+128.02 kJ\ mol^{-1}$ (d) $-12.802 kJ\ mol^{-1}$

101. Fermentation is a reaction called **[RPMT 1997]**

(a) Endothermic (b) Exothermic

(c) Isotemperature (d) Reversible

102. $8\ gm$ of CH_4 is completely burnt in air. The number of moles of water produced are **[Orissa JEE 1997]**

(a) 0.5 (b) 1

(c) 2 (d) 18

103. For the reaction $A(g) + 2B(g) \to 2C(g) + 3D(g)$, the value of ΔE at $27^o C$ is 19.0 *kcal*. The value of ΔH for the reaction would be $(R = 2.0\ cal\ K^{-1} mol^{-1})$

[Roorkee Qualifying 1998]

(a) 20.8 *kcal* (b) 19.8 *kcal*

(c) 18.8 *kcal* (d) 20.2 *kcal*

104. The enthalpy of solution of $BaCl_2(s)$ and $BaCl_2.2H_2O(s)$ are -20.6 and $8.8 kJ\ mol^{-1}$ respectively. The enthalpy change for the reaction $BaCl_2(s) + 2H_2O \to$ is

[Roorkee Qualifying 1998]

(a) 29.4 *kJ* (b) – 11.8 *kJ*

(c) – 20.6 *kJ* (d) – 29.4 *kJ*

105. The enthalpy change of a reaction does not depend on **[AIIMS 1997]**

(a) The state of reactants and products

(b) Nature of reactants and products

(c) Different intermediate reaction

(d) Initial and final enthalpy change of a reaction

106. $S + \frac{3}{2}O_2 \to SO_3 + 2x\ kcal$

$SO_2 + \frac{1}{2}O_2 \to SO_3 + y\ kcal$

Find out the heat of formation of SO_2

[AIIMS 1997; CBSE PMT 1999; KCET 1999]

(a) $2x - y$ (b) $2x + y$

(c) $x + y$ (d) $2x / y$

107. The combustion enthalpies of carbon, hydrogen and methane are $-395.5 kJ\ mol^{-1}$, $-285.8 kJ\ mol^{-1}$ and $-890.4 kJ\ mol^{-1}$ respectively at $25^o C$. The value of standard formation enthalpies of methane at that temperature is **[Pb. PMT 1998]**

(a) $890.4 kJ\ mol^{-1}$ (b) $-298.8 kJ\ mol^{-1}$

(c) $-74.7 kJ\ mol^{-1}$ (d) $-107.7 kJ\ mol^{-1}$

108. Equal volumes of methanoic acid and sodium hydroxide are mixed. If X is the heat of formation of water, then heat evolved on neutralisation is **[BHU 1998]**

(a) More than X (b) Equal to X

(c) Twice of X (d) Less than X

109. The neutralisation of a strong acid by a strong base liberates an amount of energy per mole of H^+ that **[BHU 1998]**

(a) Depends upon which acid and base are involved

(b) Depends upon the temperature at which the reaction takes place

(c) Depends upon which catalyst is used

(d) Is always the same

110. When $0.5g$ of sulphur is burnt to $SO_2, 4.6 kJ$ of heat is liberated. What is the enthalpy of formation of sulphur dioxide **[KCET 1998; AFMC 2001]**

(a) + 147.2 *kJ* (b) – 147.2 *kJ*

(c) – 294.4 *kJ* (d) + 294.4 *kJ*

111. Ozone is prepared by passing silent electric discharge through oxygen. In this reaction **[AFMC 1998]**

(a) Energy is given out

(b) Energy is absorbed

(c) Oxygen is loaded with energy

(d) Oxygen is dissociated into atoms

112. Combustion of glucose takes place according to the equation,
$C_6H_{12}O_6 + 6O_2 \rightarrow 6CO_2 + 6H_2O$,
$\Delta H = -72 kcal$. How much energy will be required for the production of 1.6 *g* of glucose (Molecular mass of glucose = 180 *g*) **[AFMC 1999]**

(a) 0.064 *kcal*
(b) 0.64 *kcal*
(c) 6.4 *kcal*
(d) 64 *kcal*

113. Given that

$$C(s) + O_2(g) \rightarrow CO_2(g), \Delta H = -394 kJ$$
$$2H_2(g) + O_2(g) \rightarrow 2H_2O(l), \Delta H = 568 kJ$$
$$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(l)$$
$$\Delta H = -892 kJ$$

Heat of formation of CH_4 is
[DCE 1999]

(a) – 70 *kJ*
(b) 71.8 *kJ*
(c) – 244 *kJ*
(d) + 782 *kJ*

114. Calculate the heat of formation of $PCl_5(s)$ from the following data

$$2P(s) + 3Cl_2(g) \rightarrow 2PCl_3(l); \Delta H = -151.8 kca$$
$$PCl_3(l) + Cl_2(g) \rightarrow PCl_5(s); \Delta H = -32.8 kcal$$

[JIPMER 1999]

(a) – 108.7 *kcal*
(b) + 108.7 *kcal*
(c) – 184.6 *kcal*
(d) + 184.6 *kcal*

115. When $50 cm^3$ of a strong acid is added to $50 cm^3$ of an alkali, the temperature rises by $5^o C$. If $250 cm^3$ of each liquid are mixed, the temperature rise would be

[KCET 1999]

(a) $5^o C$
(b) $10^o C$
(c) $25^o C$
(d) $20^o C$

116. $H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(l)$;

ΔH at 298 *K* = – 285.8 *kJ*

The molar enthalpy of vaporisation of water at 1 *atm* and $25^0 C$ is 44 *kJ*. The standard enthalpy of formation of 1 *mole* of water vapour at $25^0 C$ is **[KCET 1999]**

(a) – 241.8 *kJ*
(b) 241.8 *kJ*
(c) 329.8 *kJ*
(d) –329.8 *kJ*

117. When 4 *g* of iron is burnt to ferric oxide at constant pressure, 29.28 *kJ* of heat is evolved. What is the enthalpy of formation of ferric oxide (At. Wt. of *Fe* = 56)

[AIIMS 1999]

(a) – 81.98 *kJ*
(b) – 819.8 *kJ*
(c) – 40.99 *kJ*
(d) + 819.8 *kJ*

118. When a strong acid, strong base or their salt are dissolved in water, they are completely ionised. If a strong acid is added to a strong base, H^+ ions from the former combine with OH^- ions of the latter forming water. The formation of each water molecule liberates a certain quantity of energy and the reaction is exothermic. The heat liberated when one mole of water is formed by combining hydrochloric acid and sodium hydroxide is 13.7 *kcal*. The heat liberated when one mole of water is formed by combining sulphuric acid and sodium hydroxide is **[AMU (Engg.) 1999]**

(a) 25.5 *kcal*
(b) 8.5 *kcal*
(c) 13.7 *kcal*
(d) 34 *kcal*

119. 2.1 *g* of *Fe* combines with *S* evolving 3.77 *kJ*. The heat of formation of *FeS* in *kJ/mol* is **[AMU (Engg.) 1999]**

(a) – 1.79
(b) – 100.5
(c) – 3.77
(d) None of these

120. In the reaction: $H_2 + Cl_2 \rightarrow 2HCl, \Delta H = 194 kJ$. Heat of formation of HCl is **[KCET 2000; AFMC 2000; CPMT 2000]**

(a) + 97 *kJ*
(b) + 194 *kJ*
(c) – 194 *kJ*
(d) – 97 *kJ*

121. Enthalpy of neutralisation of acetic acid by $NaOH$ is $-50.6 kJ\ /mol.$ and the heat of neutralisation of a strong acid with a strong base is – 55.9 *kJ/mol*. What is the value of ΔH for the ionisation of CH_3COOH **[AIIMS 2000]**

(a) + 5.3 *kJ/mol*
(b) + 6.2 *kJ/mol*
(c) + 8.2 *kJ/mol*
(d) + 9.3 *kJ/mol*

122. Heat of neutralization of the acid-base reaction is 57.32 *kJ* for **[JIPMER 2000]**

(a) $HNO_3 + LiOH$
(b) $HCOOH + KOH$
(c) $HCl + NH_4OH$
(d) $CH_3COOH + NaOH$

123. The heat change for the following reaction at $298^0 K$ and at constant pressure is $+7.3 kcal$

$$A_2B(s) \rightarrow 2A(s) + 1/2\,B_2(g), \Delta H = +7.3 kcal$$

The heat change at constant volume would be

[DCE 2000]

(a) 7.3 *kcal*
(b) More than 7.3
(c) Zero
(d) None of these

124. The heat evolved in the combustion of benzene is given by the equation

$$C_6H_6(l) + 7\frac{1}{2}O_2(g) \rightarrow 3H_2O(l) + 6CO_2(g)$$
$$\Delta H = 781.0 kcal\ mol^{-1}$$

Which of the following quantities of heat energy will be evolved when 39 *g* of benzene is burnt in an open container

[MP PET 2000]

(a) 122.25 *kcal* mol^{-1} (b) 390.5 *kcal* mol^{-1}

(c) 1562.0 *kcal* mol^{-1} (d) 586.75 *kcal* mol^{-1}

125. $H_2(g) + Cl_2(g) \rightarrow 2HCl(g). \Delta H = -44 kcal$

$2Na(s) + 2HCl(g) \rightarrow 2NaCl(s) + H_2(g),$
$\Delta H = -152 kcal$

For the reaction

$$Na(s) + \frac{1}{2}Cl_2(g) \rightarrow NaCl(s), \Delta H =$$

[KCET 2000]

(a) – 108 *kcal* (b) – 196 *kcal*

(c) – 98 *kcal* (d) 54 *kcal*

126. The ΔH_f^o for $CO_2(g), CO(g)$ and $H_2O(g)$ are – 393.5, –110.5 and – 241.8*kJmol*$^{-1}$ respectively. The standard enthalpy change (in *kJ*) for the reaction $CO_2(g) + H_2(g) \rightarrow CO(g) + H_2O(g)$ is **[IIT JEE (Screening) 2000]**

(a) 524.1 (b) 41.2

(c) – 262.5 (d) – 41.2

127. Which of the following compounds will absorb the maximum quantity of heat when dissolved in the same amount of water ? The heats of solution of these compounds at $25^0 C$ in *kJ/mole* of each solute is given in brackets **[AMU (Engg.) 2000]**

(a) $HNO_3 (\Delta H = -33)$ (b) $KCl (\Delta H = +17.64)$

(c) $NH_4NO_3 (\Delta H = +25.5)$ (d) $HCl (\Delta H = -74.1)$

128. In the reaction $C + 2S \rightarrow CS_2 + \Delta H, \Delta H$ is the

[AMU (Engg.) 2000]

(a) Heat of combustion (b) Heat of neutralisation

(c) Heat of solution (d) None of these

129. The heat of formation of methane $C(s) + 2H_2(g) \rightarrow CH_4(g)$ at constant pressure is 18500 *cal* at $25^0 C$. The heat of reaction at constant volume would be **[MH CET 2000]**

(a) 17904 *cal* (b) 18202 *cal*

(c) 18798 *cal* (d) 19096 *cal*

130. The enthalpy of combustion of $C_6H_{6(l)}$ is – 3250 *kJ*. When 0.39 *g* of benzene is burnt excess of oxygen in an open vessel, the amount of heat evolved is

[KCET 2000; AFMC 2000; DCE 2000]

(a) 16.25 *J* (b) 16.25 *kJ*

(c) 32.5 *J* (d) 32.5 *kJ*

131. $C(s) + O_2(g) \rightarrow CO_2; \quad \Delta H = -94 kcal$

$$CO(g) + \frac{1}{2}O_2(g) \rightarrow CO_2; \quad \Delta H = 135.2 kcal$$

Then heat of formation of $CO(g)$ is **[DCE 2001]**

(a) – 26.4 *kcal* (b) 41.2 *kcal*

(c) 26.4 *kcal* (d) – 229.2 *kcal*

132. The heat of neutralization of HCl and $NaOH$ is

[MP PET 2001]

(a) Zero (b) – 57.3 *kJ*

(c) + 57.3 *kJ* (d) None of these

133. The following thermochemical reactions are given

$$M + \frac{1}{2}O_2 \rightarrow MO + 351.4 kJ$$

$$X + \frac{1}{2}O_2 \rightarrow XO + 90.8 kJ$$

It follows that the heat of reaction for the following process $M + XO \rightleftharpoons MO + X$ is given by

[AMU 2001]

(a) 422.2 *kJ* (b) 268.7 *kJ*

(c) – 442.2 *kJ* (d) 260.6 *kJ*

134. If the heat of combustion of carbon monoxide at constant volume and at $17^o C$ is – 283.3 *kJ*, then its heat of combustion at constant pressure $(R = 8.314 J\ degree^{-1} mol^{-1})$ **[CPMT 2001]**

(a) – 284.5 *kJ* (b) 284.5 *kJ*

(c) 384.5 *kJ* (d) – 384.5 *kJ*

135. Heat of formation of H_2O is $-188 kJ/mole$ and H_2O_2 is $-286 kJ/mole$. The enthalpy change for the reaction $2H_2O_2 \rightarrow 2H_2O + O_2$ is **[BHU 2001]**

(a) 196 *kJ* (b) – 196 *kJ*

(c) 984 *kJ* (d) – 984 *kJ*

136. The values of ΔH for the combustion of ethene and ethyne are – 341.1 and – 310.0*kcal* respectively. Which of the following is a better fuel **[BHU 2001]**

(a) C_2H_2 (b) C_2H_4

(c) Both of these (d) None of these

137. For exothermic reaction, the equilibrium constant

[JIPMER 2001]

(a) Increases with increase of *P*

(b) Decreases with increase of *P*

(c) Increases with increase of temperature

(d) Decreases with increase of temperature

138. In order to decompose 9 *g* water 142.5 *kJ* heat is required. Hence the enthalpy of formation of water is

[KCET 2001]

(a) – 142.5 *kJ* (b) + 142.5 *kJ*

(c) – 285 *kJ* (d) + 285 *kJ*

139. What is Δn for combustion of 1 mole of benzene, when both the reactants and the products are gas at 298 *K*

[Pb. PMT 2001]

(a) 0 (b) 3/2

(c) – 3/2 (d) 1/2

140. If $C + O_2 \rightarrow CO_2 + 94.2\,kcal$

$$H_2 + \frac{1}{2}O_2 \rightarrow H_2O + 68.3\,kcal$$

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O + 210.8\,kcal$$

Then the possible heat of methane will be **[UPSEAT 2001]**

(a) 47.3 *kcal* (b) 20.0 *kcal*

(c) 45.9 *kcal* (d) – 47.3 *kcal*

141. Heat of neutralization of strong acid and weak base is

[UPSEAT 2001]

(a) $57.1\,kJ\,mol^{-1}$

(b) $13.7\,kJ\,mol^{-1}$

(c) Less than $13.7\,kcal\,mol^{-1}$

(d) More than $13.7\,kcal\,mol^{-1}$

142. A system is changed from state *A* to state *B* by one path and from *B* to *A* another path. If E_1 and E_2 are the corresponding changes in internal energy, then

[Pb. PMT 2001]

(a) $E_1 + E_2 = -ve$ (b) $E_1 + E_2 = +ve$

(c) $E_1 + E_2 = 0$ (d) None of these

143. The heat evolved during the combination of 24 *g C* and 128 *g S* following the change is

$$C + S_2 \rightarrow CS_2; \Delta H = 22.0\,kcal$$

[MH CET 2001]

(a) 11 *kcal* (b) 32 *kcal*

(c) 44 *kcal* (d) 22 *kcal*

144. When the aqueous solution of 0.5 mole HNO_3 is mixed with the 0.3 mole of OH^- solution, then what will be the liberated heat (Enthalpy of neutralization is = 57.1 *kJ*)

[Kerala CET 2005]

(a) 28.5 *kJ* (b) 17.1 *kJ*

(c) 45.7 *kJ* (d) 1.7 *kJ*

(e) 2.85 *kJ*

145. A cylinder of gas is assumed to contain 11.2 *kg* of butane (C_4H_{10}). If a normal family needs 20000 *kJ* of energy per day. The cylinder will last: (Given that ΔH for combustion of butane is – 2658 *kJ*) **[AMU (Engg.) 2002]**

(a) 20 days (b) 25 days

(c) 26 days (d) 24 days

146. Compounds with high heat of formation are less stable because **[KCET 2002]**

(a) High temperature is required to synthesise them

(b) Molecules of such compounds are distorted

(c) It is difficult to synthesis them

(d) Energy rich state leads to instability

147. The heat evolved in the combustion of methane is given by the following equations:

$$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + H_2O(l);$$
$$\Delta H = -890.3\,kJ$$

How many grams of methane would be required to produce 445.15 *kJ* of heat of combustion

[AMU 2002]

(a) 4 *g* (b) 8 *g*

(c) 12 *g* (d) 16 *g*

148. Heats of combustion (ΔH^o) for $C(s), H_2(g)$ and $CH_4(g)$ are $-94, -68$ and $-213\,kcal/mol.$ respectively. The value of ΔH^o for the reaction, $C(s) + 2H_2(g) \rightarrow CH_4(g)$ is

[CBSE PMT 2002]

(a) – 85 *kcal* (b) – 111 *kcal*

(c) – 17 *kcal* (d) – 170 *kcal*

149. If the value of ΔH in a reaction is positive, then the reaction is called **[BHU 2002]**

(a) Exothermic (b) Endothermic

(c) Polymorphic (d) Polytropic

150. Enthalpy of neutralisation of NH_4OH and HCl, is numerically

[JIPMER 2002; Kurukshetra CEE 2002]

(a) $57.1\,kJ\,mol^{-1}$ (b) $< 57.1\,kJ\,mol^{-1}$

(c) $> 57.1\,kJ\,mol^{-1}$ (d) Zero

151. The heat of neutralisation will be highest in **[MP PMT 2002]**

(a) NH_4OH and CH_3COOH

(b) NH_4OH and HCl

(c) KOH and CH_3COOH

(d) KOH and HCl

152. If a mole of H_2 molecule is heated to high temperature the following reaction takes place **[Kerala (Med.) 2002]**

(a) $H_2(g) + 436\,kJ = H(g) + H(g)$

(b) $H_2(g) + 820\,kJ = 2H_2(g)$

(c) $2H_2(g) + 436\,J = 2H_2$

(d) $H_2 + H_2 = H^+ + H^+$

153. Which of the following reactions is not exothermic

[MP PET 2002]

(a) $C(s)+O_2(g)\rightarrow CO_2(g)$

(b) $C(s)+2S(s)\rightarrow CS_2(g)$

(c) $CH_4(g)+2O_2(g)\rightarrow CO_2(g)+2H_2O(l)$

(d) $CO(g)+\frac{1}{2}O_2(g)\rightarrow CO_2(g)$

154. On combustion, carbon forms two oxides CO and CO_2, Heat of formation of CO_2 gas is 94.3 *kcal* and that of *CO* is 26.0 *kcal*. Heat of combustion of carbon is **[JIPMER 2002]**

(a) 26.0 *kcal* (b) – 94.3 *kcal*

(c) 68.3 *kcal* (d) – 120.3 *kcal*

155. 1 *mole* of conc. *HCl* requires *X* moles of dilute *NaOH* for neutralisation and 1 *mole* of concentrate H_2SO_4 requires *Y moles* of small dilute $NaOH$ then which of the following reaction is true **[MH CET 2002]**

(a) $Y=\frac{1}{2}X$ (b) $X=\frac{1}{2}Y$

(c) $X=2Y$ (d) None of these

156. Which of the reaction defines ΔH_f^o **[IIT -JEE (Screening) 2003]**

(a) $C_{(\text{diamond})}+O_2(g)\rightarrow CO_2(g)$

(b) $\frac{1}{2}H_2(g)+\frac{1}{2}F_2(g)\rightarrow HF(g)$

(c) $N_2(g)+3H_2(g)\rightarrow 2NH_3(g)$

(d) $CO(g)+\frac{1}{2}O_2(g)\rightarrow CO_2(g)$

157. One gram sample of NH_4NO_3 is decomposed in a bomb calorimeter. The temperature of the calorimeter increases by 6.12 *K* the heat capacity of the system is 1.23 *kJ/g/deg.* What is the molar heat of decomposition for NH_4NO_3 **[AIIMS 2003]**

(a) – 7.53 *kJ/mol* (b) – 398.1 *kJ/mol*

(c) – 16.1 *kJ/mol* (d) – 602 *kJ/mol*

158. For which one of the following equations is $\Delta H^o_{\text{react}}$ equal to ΔH_f^o for the product **[CBSE PMT 2003]**

(a) $2CO(g)+O_2(g)\rightarrow 2CO_2(g)$

(b) $N_2(g)+O_3(g)\rightarrow N_2O_3(g)$

(c) $CH_4(g)+2Cl_2(g)\rightarrow CH_2Cl_2(l)+2HCl(g)$

(d) $Xe(g)+2F_2(g)\rightarrow XeF_4(g)$

159. Enthalpy change for a reaction does not depend upon **[AIEEE 2003]**

(a) The physical states of reactants and products

(b) Use of different reactants for the same product

(c) The nature of intermediate reaction steps

(d) The differences in initial or final temperatures of involved substances

160. $C_{\text{dia}}+O_2\rightarrow CO_2;\ \Delta H=-395.3\,kJ\ /mole$

$C_{gr}+O_2\rightarrow CO_2;\Delta H=-393.4\,kJ\ /mole$

$C_{gr}\rightarrow C_{\text{dia}};\Delta H=$ **[BHU 2003]**

(a) – 3.8 (b) – 1.9

(c) + 3.8 (d) + 1.9

161. What is the weight of oxygen that is required for the complete combustion of 2.8 *kg* of ethylene? **[BVP 2003]**

(a) 9.6 *kg* (b) 96.0 *kg*

(c) 6.4 *kg* (d) 2.8 *kg*

162. For complete neutralization of HCl with $NaOH$, the heat of neutralization is **[MP PET 2003]**

(a) $+13.70\,kJ\ mol^{-1}$ (b) $-13.70\,kJ\ mol^{-1}$

(c) $-57.32\,kJ\ mol^{-1}$ (d) $+57.32\,kJ\ mol^{-1}$

163. The heat of combustion of carbon to CO_2 is $-393.5\,kJ\ /mol$. The heat released upon formation of 35.2 g of CO_2 from carbon and oxygen gas is **[UPSEAT 2004]**

(a) $+315\,kJ$ (b) $-31.5\,kJ$

(c) $-315\,kJ$ (d) $+31.5\,kJ$

164. Which of the following equations correctly represents the standard heat of formation (ΔH_f^o) of methane **[UPSEAT 2004]**

(a) C (diamond) $+4H_{(g)}\rightarrow CH_{4(g)}$

(b) C (diamond) $+2H_{2(g)}\rightarrow CH_{4(g)}$

(c) C (graphite) $+2H_{2(g)}\rightarrow CH_{4(g)}$

(d) C (graphite) $+4H_{(g)}\rightarrow CH_{4(g)}$

165. If the heat of formation of CO_2 is $-393\,kJ$. The amount of heat evolved in the formation of 0.156 kg of CO_2 is **[MH CET 2004]**

(a) $-1357.9\ kJ$ (b) $-1275.9\,kJ$

(c) $-1572.0\,kJ$ (d) $-1165.5\,kJ$

166. Which of the following pairs has heat of neutralisation equal to 13.7 Kcals **[DCE 2003]**

(a) HCl, NH_4OH (b) HNO_3, KOH

(c) $NaOH, CH_3COOH$ (d) H_2SO_4, NH_4OH

167. The enthalpies of combustion of carbon and carbon monodie are –393.5 and –283 *kJ mol*$^{-1}$ respectivley. The enthalpy of formation of carbon monoxide per mole is **[AIEEE 2004]**

(a) $-676.5\,kJ$ (b) $676.5\,kJ$

(c) $110.5\,kJ$ (d) $-110.5\,kJ$

168. The enthalpy of combustion of methane at 25^oC is $890\,kJ$. The heat liberated when $3.2\,g$ of methane is burnt in air is **[KCET 2004]**

(a) $445\,kJ$ (b) $278\,kJ$

(c) $-890\,kJ$ (d) $178\,kJ$

169. If (i) $C+O_2 \to CO_2$, (ii) $C+1/2O_2 \to CO$, (iii) $CO+1/2O_2 \to CO_2$, the heats of reaction are $Q, -12, -10$ respectively. Then $Q=$ **[Orissa JEE 2004]**

(a) – 2 (b) 2

(c) – 22 (d) – 16

170. How much energy is released when 6 mole of octane is burnt in air ? Given ΔH_f^o for $CO_2(g)$, $H_2O(g)$ and $C_8H_{18}(l)$ respectively are – 490,– 240 and + 160 *kJ/mol* **[AIIMS 2004]**

(a) – 6.2 *kJ* (b) – 37.4 *kJ*

(c) – 35.5 *kJ* (d) – 20.0 *kJ*

171. Given : $2Fe+\frac{3}{2}O_2 \to Fe_2O_3, \Delta H = -193.4\,kJ$;

$Mg+\frac{1}{2}O_2 \to MgO, \Delta H = -140.2\,kJ$

What is the ΔH of the reaction

$Mg+Fe_2O_3 \to 3MgO+2Fe$ **[Orissa JEE 2005]**

(a) – 1802 *kJ* (b) +1802 *kJ*

(c) – 800 *kJ* (d) + 228 *kJ*

172. The enthalpy change (ΔH) for the neutralisation of $1M\ HCl$ by caustic potash in dilute solution at $298K$ is **[DPMT 2005]**

(a) 68 *kJ* (b) 65 *kJ*

(c) 57.3 *kJ* (d) 50 *kJ*

Bond energy

1. If the bond dissociation energies of XY, X_2 and Y_2 (all diatomic molecules) are in the ratio of 1 : 1 : 0.5 and $\Delta_f H$ for the formation of XY is $-200\,kJ\ mole^{-1}$. The bond dissociation energy of X_2 will be **[AIEEE 2005]**

(a) $100\,kJ\ mol^{-1}$ (b) $800\,kJ\ mol^{-1}$

(c) $300\,kJ\ mol^{-1}$ (d) $400\,kJ\ mol^{-1}$

2. Energy required to dissociate 4 *gm* of gaseous hydrogen into free gaseous atoms is 208 kcal at 25^oC. The bond energy of $H-H$ bond will be **[CPMT 1989; MP PET 2000; J & K 2005]**

(a) 104 *kcal* (b) 10.4 *kcal*

(c) 1040 *kcal* (d) 104 *cal*

3. The bond dissociation energy needed to form benzyl radical from toluene is ..... than the formation of the methyl radical from methane **[IIT 1994]**

(a) Less (b) Much

(c) Equal (d) None of the above

4. Which one of the following bonds has the highest average bond energy (*kcal/mol*) **[CPMT 1994]**

(a) $S=O$ (b) $C\equiv C$

(c) $C\equiv N$ (d) $N\equiv N$

5. The bond dissociation energies of gaseous H_2, Cl_2 and HCl are 104, 58 and 103 *kcal* respectively. The enthalpy of formation of HCl gas would be **[MP PET 1997; MP PMT 1999, 2001]**

(a) – 44 *kcal* (b) 44 *kcal*

(c) – 22 *kcal* (d) 22 *kcal*

6. The first ionization energy for *Li* is 5.4 *eV* and electron affinity of *Cl* is 3.61*eV*. The ΔH (in *kJ/mol*) for the reaction $Li(g)+Cl(g) \to Li^+ + Cl^-$ is (if resulting ions do not combine with each other) $(1\,eV = 1.6\times 10^{-19}J)$ **[MP PMT 2000, 03]**

(a) 70 (b) 100

(c) 170 (d) 270

7. Given that $C(g)+4H(g) \to CH_4(g); \Delta H = -166\,kJ$

The bond energy $C-H$ will be **[AMU 2002]**

(a) 208 *kJ/mole*

(b) – 41.6 *kJ/mole*

(c) 832 *kJ/mole*

(d) None of these

8. The $H-H$ bond energy is 430 *kJ* mol and $Cl-Cl$ bond energy is $240\,kJ\ mol^{-1}$. ΔH for HCl is $-90\,kJ$. The $H-Cl$ bond energy is about **[BVP 2003]**

(a) $180\,kJ\ mol^{-1}$ (b) $360\,kJ\ mol^{-1}$

(c) $213 kJ\ mol^{-1}$ (d) $425 kJ\ mol^{-1}$

9. If enthalpies of methane and ethane are respectively 320 and 360 calories then the bond energy of $C-C$ bond is **[UPSEAT 2003]**

(a) 80 *calories* (b) 40 *calories*

(c) 60 *calories* (d) 120 *calories*

10. If the bond energies of $H-H$, $Br-Br$ and HBr are 433, 192 and 364 $kJ\ mol^{-1}$ respectively, the ΔH^o for the reaction, $H_2(g)+Br_2(g)\rightarrow 2HBr(g)$ is **[CBSE PMT 2004]**

(a) + 261 *kJ* (b) – 103 *kJ*

(c) – 261 *kJ* (d) + 103 *kJ*

Free energy and Work function

1. The free energy change for a reversible reaction at equilibrium is **[NCERT 1984; Kurukshetra CEE 1998; AMU 1999]**

(a) Large positive (b) Small negative

(c) Small positive (d) 0

2. For a spontaneous change, free energy change ΔG is **[MNR 1983; BHU 1981, 95; AMU 1999; DCE 2000, 01; BHU 2000; MP PMT 2003]**

(a) Positive

(b) Negative

(c) Zero

(d) Can be positive or negative

3. A minus sign of the free energy change denotes that

(a) The reaction tends to proceed spontaneously

(b) The reaction is non-spontaneous

(c) The system is in equilibrium

(d) The reaction is very much unlikely

4. The relation between ΔG and ΔH is **[MP PMT 1994, 95, 97; AFMC 1997; Kurukshetra CEE 1998]**

(a) $\Delta H=\Delta G-T\Delta S$ (b) $\Delta G=\Delta H-T\Delta S$

(c) $T\Delta S-\Delta G=\Delta H$ (d) $\Delta H=T\Delta G+\Delta S$

5. At 300 *K*, the reactions which have following values of thermodynamic parameters occur spontaneously **[Roorkee 1999]**

(a) $\Delta G^o=-400\ kJ\ mol^{-1}$

(b) $\Delta H^o=200\ kJ\ mol^{-1},\ \Delta S^o=-4\ JK^{-1}mol^{-1}$

(c) $\Delta H^o=-200 kJ\ mol^{-1},\ \Delta S^o=4 JK^{-1}mol^{-1}$

(d) $\Delta H^o=200 J\ mol^{-1},\ \Delta S^o=40 JK^{-1}mol^{-1}$

6. The relation $\Delta G=\Delta H-T\Delta S$ was given by **[MP PMT 2000; KCET 2002]**

(a) Boltzmann (b) Faraday

(c) Gibbs–Helmholtz (d) Thomson

7. For precipitation reaction of Ag^+ ions with $NaCl$, which of the following statements is correct **[CPMT 1988]**

(a) ΔH for the reaction is zero

(b) ΔG for the reaction is zero

(c) ΔG for the reaction is negative

(d) $[\Delta G]=[\Delta H]$

8. At constant pressure and temperature, the direction to the result of any chemical reaction is where, there is less amount of

(a) Entropy (b) Enthalpy

(c) Gibb's free energy (d) None of the above

9. The dependence of Gibbs free energy on pressure for an isothermal process of an ideal gas is given by **[MP PET 1996]**

(a) $\Delta G_T=nRT\ln\frac{P_2}{P_1}$ (b) $\Delta G_T=nRT\ln\frac{V_2}{V_1}$

(c) $\Delta G_T=nRT\log\frac{P_1}{P_2}$ (d) $\Delta G_T=nRT\log\frac{V_2}{V_1}$

10. For the change $H_2O(l)\rightarrow H_2O(g); P=1\,atm$, $T=373K$, the free energy change $\Delta G=0$. This indicates that

(a) $H_2O(l)$ is in equilibrium with $H_2O(g)$

(b) Water boils spontaneously at $373K$

(c) Water does not boil spontaneously at $373K$

(d) Condensation of water vapour occurs spontaneously at $373K$

11. What is the free energy change ΔG when $1.0 mole$ of water at 100^oC and $1 atm$ pressure is converted into steam at 100^oC and $1 atm$ pressure **[MP PET/PMT 1998]**

(a) $540 cal$ (b) $-9800 cal$

(c) $9800 cal$ (d) $0 cal$

12. ΔG^o for the reaction $X+Y\rightleftharpoons Z$ is – 4.606 *kcal*. The value of equilibrium constant of the reaction at 227^oC is $(R=2.0\,cal.mol^{-1}K^{-1})$ **[Roorkee 1999]**

(a) 100 (b) 10

(c) 2 (d) 0.01

13. The standard enthalpy of the decomposition of N_2O_4 to NO_2 is 58.04 *kJ* and standard entropy of this reaction is 176.7 *J/K*. The standard free energy change for this reaction at 25^oC is **[AIIMS 1999]**

(a) 539 *kJ*
(b) – 539 *kJ*
(c) – 5.39 *kJ*
(d) 5.39 *kJ*

14. Spontaneity of a chemical reaction is decided by the negative change in **[MP PET 2001]**

(a) Internal energy
(b) Enthalpy
(c) Entropy
(d) Free energy

15. For a reaction at 25^0C enthalpy change and entropy changes are $-11.7\times10^3 J\ mol^{-1}$ and $-105 J\ mol^{-1}K^{-1}$ respectively. What is the Gibbs free energy **[BHU 2001]**

(a) 15.05 *kJ*
(b) 19.59 *kJ*
(c) 2.55 *kJ*
(d) 22.55 *kJ*

16. Born-Haber cycle is used to determine **[UPSEAT 2001]**

(a) Crystal energy
(b) Electron affinity
(c) Lattice energy
(d) All of these

17. Gibbs free energy *G*, enthalpy *H* and entropy *S* are interrelated as in **[MP PMT 2002]**

(a) $G=H+TS$
(b) $G=H-TS$
(c) $G-TS=H$
(d) $G=S=H$

18. The essential condition for the feasibility of a reaction is that **[JIPMER 2002]**

(a) The reaction should be exothermic
(b) The entropy of products must be larger than that of reactants
(c) The reaction is to be accompanied with free energy decrease
(d) The reaction has to possess high activation energy

19. The correct relationship between free energy change in a reaction and the corresponding equilibrium constant K_c is **[AIEEE 2003]**

(a) $\Delta G=RT\ln K_c$
(b) $-\Delta G=RT\ln K_c$
(c) $\Delta G^o=RT\ln K_c$
(d) $-\Delta G^o=RT\ln K_c$

20. In an irreversible process taking place at constant *T* and *P* and in which only pressure-volume work is being done, the change in Gibbs free energy (dG) and change in entropy (dS), satisfy the criteria **[AIEEE 2003]**

(a) $(dS)_{V,E}<0,(dG)_{T,P}<0$
(b) $(dS)_{V,E}>0,(dG)_{T,P}<0$
(c) $(dS)_{V,E}=0,(dG)_{T,P}=0$
(d) $(dS)_{V,E}=0,(dG)_{T,P}>0$

21. The densities of graphite and diamond at 298 *K* are 2.25 and 3.31 $g\ cm^{-3}$, respectively. If the standard free energy difference (ΔG^o) is equal to 1895 $J\ mol^{-1}$, the pressure at which graphite will be transformed diamond at 298 *K* is **[CBSE PMT 2003]**

(a) $9.92\times10^5 Pa$
(b) $9.92\times10^8 Pa$
(c) $9.92\times10^7 Pa$
(d) $9.92\times10^6 Pa$

22. The free energy change for the following reactions are given below,

$$C_2H_2(g)+\frac{5}{2}O_2(g)\rightarrow$$
$$2CO_2(g)+H_2O(l);\ \Delta G^o=-1234\,kJ$$
$$C(s)+O_2(g)\rightarrow CO_2(g)\ \Delta G^o=-394\,kJ$$
$$H_2(g)+\frac{1}{2}O_2(g)\rightarrow H_2O(l)\ \ \Delta G^o=-237kJ$$

What is the standard free energy change for the reaction $H_2(g)+2C(s)\rightarrow C_2H_2(g)$ **[Kerala (Med.) 2002]**

(a) – 209 *kJ*
(b) – 2259 *kJ*
(c) + 2259 *kJ*
(d) 209 *kJ*

23. The equilibrium concentration of the species in the reaction $A+B\equiv C+D$ are 3, 5, 10 and 15 $mole\,L^{-1}$ respectively at $300\,K$ the ΔG for the reaction is **[Pb. PMT 2004]**

(a) 13.81
(b) – 1381.8
(c) – 138.18
(d) 1391.6

24. Gibb's free enrgy (G) is defined as **[Pb. CET 2001]**

(a) $\Delta G=\Delta H-T\Delta S$
(b) $\Delta G=\Delta H+\frac{T}{\Delta S}$
(c) $\Delta H=\Delta G-T\Delta S$
(d) $\Delta G=\Delta H+T.C_p$

25. Standard enthalpy and standard entropy changes for the oxidation of ammonia at $298\,K$ are $-382.64\,kJ\ mol^{-1}$ and $-145.6\,JK^{-1}mol^{-1}$, respectively. Standard Gibbs energy change for the same reaction at $298\,K$ is **[CBSE PMT 2004]**

(a) – 439.3 kJ mol^{-1}
(b) – 523.2 $kJ\ mol^{-1}$
(c) – 221.1 $kJ\ mol^{-1}$
(d) – 339.3 $kJ\ mol^{-1}$

26. For spontaneity of a cell, which is correct **[Orissa JEE 2004]**

(a) $\Delta G=0,\Delta E=0$
(b) $\Delta G=-ve,\Delta E=0$
(c) $\Delta G=+ve,\Delta E=+ve$
(d) $\Delta G=-ve,\Delta E=+ve$

27. The free energy for a reaction having $\Delta H = 31400\, cal$, $\Delta S = 32\, cal\, K^{-1}\, mol^{-1}$ at $1000^o C$ is **[Orissa JEE 2005]**

(a) – 9336 *cal* (b) – 7386 *cal*

(c) –1936 *cal* (d) + 9336 *cal*

28. The ΔH and ΔS for a reaction at one atmospheric pressure are +30.558 *kJ* and $0.066\, kJk^{-1}$ respectively. The temperature at which the free energy change will be zero and below of this temperature the nature of reaction would be **[Kerala CET 2005]**

(a) 483 *K*, spontaneous

(b) 443 *K*, non-spontaneous

(c) 443 *K*, spontaneous

(d) 463 *K*, non-spontaneous

(e) 463 *K*, spontaneous

CT Critical Thinking

Objective Questions

1. Adsorption of gases on solid surface is generally exothermic because **[IIT JEE (Screening) 2004]**

(a) Enthalpy is positive (b) Entropy decreases

(c) Entropy increases (d) Free energy increase

2. Two mole of an ideal gas is expanded isothermally and reversibly from 1 litre ot 10 litre at $300K$. The enthalpy change (in kJ) for the process is

[IIT JEE (Screening) 2004]

(a) 11.4 *kJ* (b) –11.4 *kJ*

(c) 0 *kJ* (d) 4.8 *kJ*

3. Heat of neutralization of strong acid against strong base is constant and is equal to

[EAMCET 1980; AFMC 1989; DPMT 1991; MP PET 1999; BHU 1999; MP PMT 1995]

(a) 13.7 *kcal* (b) 57 *kJ*

(c) $5.7 \times 10^4\, J$ (d) All of the above

4. The value of heat generated when 36.5 *gm* HCl and 40 *gm* of $NaOH$ reacts during neutralization

[NCERT 1984; CPMT 1993]

(a) 76.5 *kcal* (b) 13.7 *kcal*

(c) More than 13.7 *kcal* (d) 108 kcal

5. When a gas undergoes adiabatic expansion, it gets cooled due to **[DCE 2002]**

(a) Loos of kinetic energy

(b) Fall in temperature

(c) Decrease in velocity

(d) Energy used in doing work

6. The heat content of a system is called

(a) Internal energy (b) Entropy

(c) Free energy (d) Enthalpy

7. To calculate the amount of work done in joules during reversible isothermal expansion of an ideal gas, the volume must be expressed in **[KCET (Med.) 2001]**

(a) m^3 only (b) dm^3 only

(c) cm^3 only (d) Any one of them

8. In an isobaric process, the ratio of heat supplied to the system (dQ) and work done by the system (dW) for diatomic gas is **[AFMC 2002]**

(a) 1 : 1 (b) 7 : 2

(c) 7 : 5 (d) 5 : 7

9. The enthalpy change for the reaction of 50.00 ml of ethylene with 50.00 ml of H_2 at 1.5 atm pressure is $\Delta H = -0.31\, kJ$. The value of ΔE will be **[DPMT 2004]**

(a) –0.3024 *kJ* (b) 0.3024 *kJ*

(c) 2.567 *kJ* (d) –0.0076 *kJ*

10. Enthalpy of solution of $NaOH$ (solid) in water is $-41.6\, kJ\, mol^{-1}$. When $NaOH$ is dissolved in water, the temperature of water **[UPSEAT 2004]**

(a) Increase (b) Decreases

(c) Does not change (d) Fluctuates indefinitely

11. In which of the following entropy decreases ?

[CPMT 1988, 94; MP PMT 2000]

(a) Crystallization of sucrose from solution

(b) Rusting of iron

(c) Melting of ice

(d) Vaporization of camphor

12. For conversion *C* (graphite) → *C* (diamond) the ΔS is

[MP PMT 2001; MP PET 2003]

(a) Zero (b) Positive

(c) Negative (d) Unknown

13. For a reaction $\Delta H = 9.08\, kJ\, mol^{-1}$ and

$\Delta S = 35.7\, JK^{-1} mol^{-1}$

Which of the following statements is correct for the reaction

[AMU (Engg.) 2000]

(a) Reversible and Isothermal

(b) Reversible and Exothermic

(c) Spontaneous and Endothermic

(d) Spontaneous and Exothermic

14. For a reaction to occur spontaneously **[CBSE PMT 1995]**

(a) $(\Delta H - T\Delta S)$ must be negative

(b) $(\Delta H + T\Delta S)$ must be negative

(c) ΔH must be negative

(d) ΔS must be negative

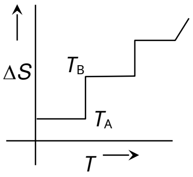
15. The total amount of energy in the universe is fixed, but **[AMU (Engg.) 1999]**

(a) Disorder is increasing (b) Lightning is increasing

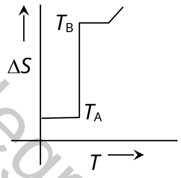
(c) Matter is increasing (d) Gravitation is decreasing

16. If for a given substance melting point is T_B and freezing point is T_A, then correct variation shown by graph between entropy change and temperature is **[DCE 2001]**

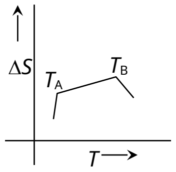
(a)



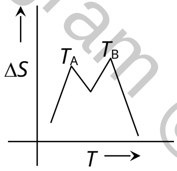
(b)



(c)



(d)



17. In endothermic reaction, the value of change in enthalpy (ΔH) is **[Pb. CET 2001]**

(a) Positive (b) Negative

(c) Zero (d) None of these

18. Which of the following would be expected to have the largest antropy per mole **[MP PMT 2004]**

(a) $SO_2Cl_2(s)$ (b) $SO_2Cl_2(g)$

(c) $SO_2Cl_2(l)$ (d) $SO_2(g)$

19. The enthalpies of formation of Al_2O_3 and Cr_2O_3 are $-1596 kJ$ and $-1134 kJ$ respectively. ΔH for the reaction $2Al + Cr_2O_3 \rightarrow 2Cr + Al_2O_3$ is **[KCET 2003]**

(a) $-2730 kJ$ (b) $-462 kJ$

(c) $-1365 kJ$ (d) $+2730 kJ$

20. Heat of reaction at constant volume is measured in the apparatus

(a) Bomb calorimeter (b) Calorimeter

(c) Pyknometer (d) Pyrometer

21. Which of the following gas has the highest heat of combustion

(a) Methane (b) Ethane

(c) Ethylene (d) Acetylene

22. The amount of heat measured for a reaction in a bomb calorimeter is **[AIIMS 1991]**

(a) ΔG (b) ΔH

(c) ΔE (d) $P\Delta V$

23. For an endothermic reaction where ΔH represents the enthalpy of the reaction in *kJ/mole*, the minimum value for the energy of activation will be **[IIT JEE 1992; MP PET 1993]**

(a) Less than ΔH (b) Zero

(c) More than ΔH (d) Equal to ΔH

24. The heat of neutralization of a strong acid by a strong base is nearly equal to **[MP PET 1993; BCECE 2005]**

(a) + 57.32 *J* (b) – 57.32 *kJ*

(c) + 13.7 *J* (d) – 13.7 *kJ*

25. A Beckmann thermometer is used to measure **[Kurukshetra CEE 2002]**

(a) High temperature (b) Low temperature

(c) Normal temperature (d) All temperature

26. The heat required to raise the temperature of a body by 1 *K* is called **[AIEEE 2002]**

(a) Specific heat (b) Thermal capacity

(c) Water equivalent (d) None of these

27. Mechanical work is specially important in system that contain **[Kerala (Med.) 2002]**

(a) Solid-liquid (b) Liquid-liquid

(c) Solid-solid (d) Amalgam

(e) Gases

28. "The quantity of heat which must be supplied to decompose a compound into its element is equal to the heat evolved during the formation of that compound from the elements." This statement is known as

(a) Hess's law

(b) Joule's law

(c) Le–chatelier's principle

(d) Lavoiser and Laplace law

29. Hess law deals with **[BHU 1979]**

(a) Changes in heat of reaction

(b) Rate of reaction

(c) Equilibrium constant

(d) Influence of pressure on volume of a gas

30. For which one of the following reactions, ΔH is not equal to ΔE **[IIT JEE 1995]**

(a) $H_{2(g)} + I_{2(g)} \rightleftharpoons 2HI_{(g)}$

(b) $C_{(s)} + O_{2(g)} \rightleftharpoons CO_{2(g)}$

(c) $N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)}$

(d) $HCl_{(aq)} + NaOH_{(aq)} \rightleftharpoons NaCl_{(aq)} + H_2O$

31. The heat liberated when 1.89 *g* of benzoic acid is burnt in a bomb calorimeter at 25^0C increases the temperature of 18.94 *kg* of water by 0.632^0C .If the specific heat of water at 25^0C is 0.998 *cal/g-deg*, the value of the heat combustion of benzoic acid is **[CPMT 1999; BHU 2000]**

(a) 771.1 *kcal*
(b) 871.2 *kcal*
(c) 881.1 *kcal*
(d) 981.1 *kcal*

32. For a hypothetic reaction $A \to B$, the activation energies for forward and backward reactions are 19 *kJ/mole* and 9 *kJ/mole* respectively. The heat of reaction is

[CBSE PMT 2000]

(a) 28 *kJ*
(b) 19 *kJ*
(c) 10 *kJ*
(d) 9 *kJ*

33. The enthalpy of neutralization of HCN by $NaOH$ is $-12.13 kJ\ mol^{-1}$. The enthalpy of ionisation of HCN will be

[BHU 1997]

(a) 4.519 *kJ*
(b) 45.10 *kJ*
(c) 451.9 *kJ*
(d) 45.19 *kJ*

34. In thermodynamics, a process is called reversible when

[AIIMS 2001]

(a) Surroundings and system change into each other
(b) There is no boundary between system and surroundings
(c) The surroundings are always in equilibrium with the system
(d) The system changes into the surroundings spontaneously

35. Which of the following unit represents largest amount of energy **[AMU 2001]**

(a) *Calorie*
(b) *Joule*
(c) *Erg*
(d) *Electron volt*

36. Which of the following will have the highest bond energy

[MP PMT 1990]

(a) F_2
(b) Cl_2
(c) Br_2
(d) I_2

37. $C_{(graphite)} + O_2(g) \to CO_2(g)$

$\Delta H = -94.05 kcal\,mol^{-1}$

$C_{(diamond)} + O_2(g) \to CO_2(g);$

$\Delta H = -94.50 kcal\,mol^{-1}$

therefore **[DPMT 2001]**

(a) $C_{(graphite)} \to C_{(diamond)};$

$\Delta H^o_{298K} = -450 cal\,mol^{-1}$

(b) $C_{(diamond)} \to C_{(graphite)};$

$\Delta H^o_{298K} = +450 cal\,mol^{-1}$

(c) Graphite is the stabler allotrope
(d) Diamond is harder than graphite

38. Enthalpy of formation of two compounds *x* and *y* are – 84 *kJ* and – 156 *kJ* respectively. Which of the following statements is correct **[CBSE PMT 2001]**

(a) *x* is more stable than *y*
(b) *x* is less stable than *y*
(c) Both *x* and *y* are unstable
(d) *x* and *y* are endothermic compounds

39. For the process dry ice $\longrightarrow CO_2(g)$ **[KCET 2000]**

(a) ΔH is positive while $\Delta \rho$ is negative
(b) Both ΔH and $\Delta \rho$ are negative
(c) Both ΔH and $\Delta \rho$ are positive
(d) ΔH is negative while $\Delta \rho$ is positive

40. For melting of 3 moles of water at 0^oC the ΔG^o is

[MP PMT 2001]

(a) Zero
(b) + *ve*
(c) – *ve*
(d) Unpredictable

41. The equilibrium constant of a reaction at $298K$ is 5×10^{-3} and at $1000K$ is 2×10^{-5}. What is the sign of ΔH for the reaction **[Pb. CET 1998]**

(a) $\Delta H = 0$
(b) ΔH is negative
(c) ΔH is positive
(d) None of these

42. Which of the following has lowest fusion temperature

[MP PET 2003]

(a) Naphthalene
(b) Diamond
(c) *NaCl*
(d) *Mn*

43. Consider the reactions

$C(s) + 2H_2(g) \to CH_4(g), \Delta H = -x\,kcal$

$C(g) + 4H(g) \to CH_4(g), \Delta H = -x_1\,kcal$

$CH_4(g) \to CH_3(g) + H(g), \Delta H = +y\,kcal$

The bond energy of $C-H$ bond is **[JIPMER 1997]**

(a) $y\,kcal\,mol^{-1}$
(b) $x_1\,kcal\,mol^{-1}$
(c) $x/4\,kcal\,mol^{-1}$
(d) $x_1/4\,kcal\,mol^{-1}$

44. Given the bond energies $N \equiv N$, $H-H$ and $N-H$ bonds are $945, 436$ and $391 kJ\ mole^{-1}$ respectively, the enthalpy of the following reaction $N_2(g) + 3H_2(g) \to 2NH_3(g)$ is

[EAMCET 1992; JIPMER 1997]

(a) $-93kJ$ (b) $102kJ$

(c) $90kJ$ (d) $105kJ$

45. The relation between ΔG and E for a cell is $\Delta G = -nFE$; the cell reaction will be spontaneous if **[MP PET 1995]**

(a) G is negative (b) G is positive

(c) E is negative (d) E is positive

46. Which of the following is not a correct statement? **[AMU (Engg.) 2002]**

(a) When ΔG is negative, the process is spontaneous

(b) When ΔG is zero, the process is in a state of equilibrium

(c) When ΔG is positive, the process is non-spontaneous

(d) None of these

47. If at 298 *K* the bond energies of $C-H, C-C$, $C=C$ and $H-H$ bonds are respectively 414, 347, 615 and 435 *kJ* mol^{-1}, the value of enthalpy change for the reaction $H_2C=CH_2(g)+H_2(g)\rightarrow H_3C-CH_3(g)$ at 298 *K* will be **[AIEEE 2003]**

(a) + 250 *kJ* (b) – 250 *kJ*

(c) + 125 *kJ* (d) – 125 *kJ*

48. The equation

$$\frac{1}{2}H_2+\frac{1}{2}Cl_2\rightarrow HCl \qquad (\Delta H_{298}=-22060kcal)$$

means **[CMC Vellore 1991]**

(a) The heat absorbed when one gram molecule of HCl is formed from its elements at 25^oC is 22.060 *kcal*

(b) The heat given out when one gram molecule of HCl is formed from its elements at 298 *K* is 22.060 *kcal*

(c) The heat absorbed when one atom of hydrogen reacts with one atom of chlorine to form one molecule of HCl at 25^oC and one atmospheric pressure is 22.060 *kcal*

(d) The heat absorbed when one gram equivalent of HCl is formed from its elements at 298 *K* is 22.060 *kcal*

(e) The intrinsic heat of one molecule of HCl is 22.060 *kcal* more than the intrinsic heats of one atom of hydrogen and one atom of chlorine

49. The $H_2O(g)$ molecule dissociates as

(i) $H_2O(g)\rightarrow H(g)+OH(g); \Delta H=490kJ$

(ii) $OH(g)\rightarrow H(g)+O(g); \Delta H=424kJ$

The average bond energy (in *kJ*) for water is

(a) 490 (b) 424

(c) 914 (d) 914/2

50. When $50cm^3$ of $0.2\,N\,H_2SO_4$ is mixed with $50cm^3$ of $1\,N\,KOH$, the heat liberated is **[KCET 2004]**

(a) 11.46 *kJ* (b) 57.3 *kJ*

(c) 573 *kJ* (d) 573 *J*

51. Following reaction occurring in an automobile $2C_8H_{18}(g)+25O_2(g)\rightarrow 16CO_2(g)+18H_2O(g)$. The sign of $\Delta H, \Delta S$ and ΔG would be **[CBSE PMT 1994; KCET 1999]**

(a) +, –, + (b) –, +, –

(c) –, +, + (d) +, +, –

52. For the reaction

$$H_2(g)+\frac{1}{2}O_2(g)\rightarrow H_2O(l), \Delta H=-285.8\ kJ\ mol^{-1}$$

$\Delta S=-0.163kJ\ mol^{-1}K^{-1}$. What is the value of free energy change at 27^oC for the reaction **[KCET 1999]**

(a) $-236.9kJ\ mol^{-1}$ (b) $-281.4kJ\ mol^{-1}$

(c) $-334.7kJ\ mol^{-1}$ (d) $+334.7kJ\ mol^{-1}$

Assertion & Reason

For AIIMS Aspirants

Read the assertion and reason carefully to mark the correct option out of the options given below :

(a) If both assertion and reason are true and the reason is the correct explanation of the assertion.
(b) If both assertion and reason are true but reason is not the correct explanation of the assertion.
(c) If assertion is true but reason is false.
(d) If the assertion and reason both are false.
(e) If assertion is false but reason is true.

1. Assertion : The enthalpy of formation of gaseous oxygen molecules at $298K$ and under pressure of $1\,atm$ is zero.

Reason : The entropy of formation of gaseous oxygen molecules under the same condition is zero. **[AIIMS 1996]**

2. Assertion : We feel cold on touching the ice.

Reason : Ice is a solid form of water. **[AIIMS 1999]**

3. Assertion : Entropy of ice is less than water.

Reason : Ice have cage like structure. **[AIIMS 2000]**

4. Assertion : The heat absored during the isothermal expansion of an ideal gas against vacuum is zero.

Reason : The volume occupied by the molecules of an ideal gas is zero. **[AIIMS 2002]**

5. Assertion : Absolute values of internal energy of substance can not be determined.

Reason : It is impossible to determine exact values of constituent energies of the substances.

[AIIMS 2002]

6. Assertion : Mass and volume are extensive properties.

Reason : Mass / volume is also an extensive parameter. **[AIIMS 2002]**

7. Assertion : Molar entropy of vaporization of water is different from ethanol.

Reason : Water is more polar than ethanol.

8. Assertion : The increase in internal energy (ΔE) for the vaporiation of one mole of water at 1 atm and 373K is zero.

Reason : For all isothermal processes $\Delta E = 0$.

[AIIMS 2003]

9. Assertion : ΔH and ΔE are almost the same for the reaction. $N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$.

Reason : All reactants and products are gases.

[AIIMS 2003]

10. Assertion : The enthalpies of neutralisation of strong acids and strong bases are always same.

Reason : Neutralisation is heat of formation of water.

[AIIMS 1996]

11. Assertion : Zeroth law can also be termed as law of thermal equilibirum.

Reason : Two objects in thermal equilibrium with the third one, are in thermal equilibrium with each other.

12. Assertion : There is no reaction known for which ΔG is positive, yet it is spontaneous.

Reason : For photochemical reactions ΔG is negative.

13. Assertion : Heat of neutralisation of perchloric acid, $HClO_4$ with $NaOH$ is same as is that of HCl with $NaOH$.

Reason : Both HCl and $HClO_4$ are strong acids.

14. Assertion : Heat absorbed in a reaction at constant temperature and constant volume is $-\Delta G$.

Reason : ΔG should be negative for the reaction to be spontaneous.

15. Assertion : T, P and V are state variables or state functions.

Reason : Their values depends on the state of the system and how it is reached.

16. Assertion : Internal energy is an extensive property.

Reason : Internal energy depends upon the amount of the system.

17. Assertion : For the combustion reactions, the value of ΔH is always negative.

Reason : The combustions reactions are always endothermic.

18. Assertion : For an isothermal reversible process $Q = -w$ i.e. work done by the system equals the heat absorbed by the system.

Reason : Enthalpy change (ΔH) is zero for isothermal process.

19. Assertion : Enthalpy of formation of graphite is zero but of diamond is not zero.

Reason : Enthalpy of formation of most stable allotrope is taken as zero.

20. Assertion : If a refrigerator's door is kept open room gets cooled.

Reason : Material kept inside the refrigerator reamins cool.

21. Assertion : Enthalpy and entropy of any elementary substance in the standard state are taken as zero.

Reason : At zero degree absolute, the constituent particles become completely motionless.

22. Assertion : A process is called adiabatic if the system does not exchange heat with the surroundings.

Reason : It does not involve increase or decreae in temperature of the system.

Answers

Basic concepts

1	b	2	d	3	b	4	c	5	c
6	d	7	d	8	c	9	c	10	c

11	d	12	d	13	a	14	c	15	b
16	b	17	d	18	a	19	b	20	b
21	d	22	b	23	c	24	c	25	d
26	c	27	c	28	c				

First law of thermodynamics and Hess law

1	d	2	b	3	a	4	b	5	c
6	a	7	c	8	a	9	b	10	d
11	b	12	c	13	c	14	c	15	b
16	b	17	c	18	b	19	c	20	a
21	c	22	c	23	a	24	a	25	b
26	a	27	a	28	a	29	bc	30	c
31	b	32	c	33	b	34	a	35	c
36	b	37	c	38	b	39	d	40	c
41	d	42	a	43	c	44	a	45	c
46	c	47	b	48	c	49	d	50	b
51	a	52	d	53	b	54	c	55	a
56	b	57	d	58	d				

IInd & IIIrd Law of thermodynamics and Entropy

1	c	2	d	3	d	4	b	5	b
6	d	7	a	8	d	9	b	10	c
11	c	12	c	13	d	14	d	15	c
16	b	17	d	18	a	19	a	20	a
21	d	22	c	23	a	24	d	25	c
26	d	27	c	28	b	29	c	30	b
31	b	32	d	33	d	34	a	35	c
36	b	37	c	38	a	39	c	40	c
41	c	42	c	43	c	44	d	45	b
46	a	47	c	48	d	49	d	50	c
51	c	52	b	53	a	54	c	55	c
56	c	57	a	58	b	59	d	60	b
61	b	62	d	63	a	64	c	65	a
66	c	67	b	68	b				

Heat of reaction

1	b	2	b	3	d	4	d	5	d
6	b	7	c	8	a	9	b	10	a
11	bcd	12	a	13	d	14	b	15	c
16	a	17	b	18	a	19	b	20	c
21	c	22	a	23	d	24	c	25	c
26	b	27	b	28	b	29	a	30	c
31	a	32	a	33	d	34	b	35	b
36	a	37	a	38	d	39	b	40	b
41	c	42	c	43	b	44	b	45	b
46	b	47	a	48	c	49	e	50	b
51	a	52	b	53	c	54	c	55	b
56	c	57	c	58	d	59	c	60	b
61	d	62	c	63	b	64	a	65	b
66	b	67	a	68	c	69	a	70	d
71	a	72	b	73	d	74	c	75	b
76	b	77	a	78	d	79	d	80	a
81	b	82	b	83	a	84	b	85	b
86	c	87	a	88	b	89	d	90	d
91	a	92	c	93	b	94	a	95	d
96	d	97	c	98	a	99	c	100	c
101	b	102	c	103	d	104	d	105	c
106	a	107	c	108	d	109	d	110	c
111	a	112	b	113	a	114	a	115	a
116	a	117	b	118	c	119	b	120	a
121	a	122	a	123	d	124	b	125	b
126	b	127	c	128	d	129	d	130	b
131	d	132	b	133	d	134	a	135	a
136	a	137	d	138	c	139	d	140	b
141	c	142	d	143	c	144	b	145	c
146	d	147	b	148	c	149	b	150	b
151	d	152	a	153	b	154	b	155	b
156	b	157	a	158	d	159	c	160	d
161	a	162	c	163	c	164	c	165	c
166	b	167	d	168	d	169	c	170	b
171	a	172	c						

Bond energy

1	b	2	a	3	a	4	d	5	c
6	c	7	b	8	d	9	b	10	b

Free energy and Work function

1	d	2	b	3	a	4	b	5	acd
6	c	7	c	8	c	9	a	10	a
11	d	12	a	13	d	14	d	15	b
16	d	17	b	18	c	19	d	20	b
21	b	22	d	23	b	24	a	25	d
26	d	27	a	28	d				

Critical Thinking Questions

1	b	2	c	3	d	4	b	5	b
6	d	7	d	8	b	9	a	10	a
11	a	12	c	13	c	14	a	15	a
16	a	17	a	18	d	19	b	20	a
21	b	22	c	23	c	24	b	25	b
26	b	27	e	28	d	29	a	30	c
31	a	32	c	33	d	34	ac	35	a
36	b	37	c	38	b	39	c	40	a
41	b	42	a	43	a	44	a	45	d
46	d	47	d	48	b	49	d	50	d
51	b	52	a						

Assertion & Reason

1	b	2	b	3	b	4	c	5	a
6	b	7	b	8	a	9	b	10	a
11	a	12	d	13	a	14	e	15	c
16	a	17	c	18	b	19	a	20	e
21	c	22	c						

Answers and Solutions

Basic concepts

1. (b) Internal energy of an ideal gas is a function of temperature only.

2. (d) In cyclic process, a system in a given state goes through a series of different processes, but in the end returns to its initial state.

4. (c) $\Delta E = 0$ for isothermal reversible cycle.

5. (c) In isolated system neither exchange of matter nor exchange of energy is possible with surroundings.

9. (c) It is the definition of calorific value.

11. (d) When a real gas is forced through a porous plug into a region of low pressure, it is found that due to expansion, the gas on the side of low pressure gets cooled.

The phenomenon of producing lowering of temperature when a gas is made to expand adiabatically from a region of high pressure into a region of low pressure is known as Joule-Thomson effect.

12. (d) In isothermal reversible process ideal gas has constant volume and so $\Delta E = 0$ and $\Delta H = \Delta E = 0$.

13. (a) The compressor has to run for longer time releasing more heat to the surroundings.

14. (c) This is based on Joule-Thomson effect.

15. (b) Enthalpy is an extensive property.

16. (b) $dV = 0$ for an isochoric process.

17. (d) Total energy of an isolated system is constant.

18. (a) For isochoric process $\Delta V = 0$ so $q_V = \Delta E$ i.e. heat given to a system under constant volume is used up in increasing ΔE .

19. (b) The less energy of a system and more is its stability.

20. (b) The functions whose value depends only on the state of a system are known as state functions.

21. (d) For adiabatic process $q = 0$.

22. (b) The intensive property is mass/volume.

23. (c) Volume is not an intensive property.

24. (c) An isolated system neither shows exchange of heat nor matter with surroundings.

25. (d) ΔQ is not a state function.

26. (c) For adiabatic process $\Delta Q = 0$.

27. (c) Work is not a state function as during a process its value depends on the path followed. The value of enthalpy, internal energy and entropy depends on the state and not on the path followed to get that state, hence these are state functions.

28. (c) Surface tension is an intensive property which do not depend upon the quantity of matter present in the system.

First law of thermodynamics and Hess law

1. (d) First low of thermodynamics is also known as Law of conservation of mass and energy.

2. (b) Formation of CO_2 from CO is an exothermic reaction; heat is evolved from the system, *i.e.*, energy is lowered. Thus, exothermic reactions occur spontaneously on account of decrease in enthapy of system. Thus, $\Delta E > \Delta H$.

4. (b) $\Delta H = \Delta E + P\Delta V$.

5. (c) $\Delta n_g = 1 - \frac{3}{2} = \frac{-1}{2}$, As Δn_g is negative, thus $\Delta H < \Delta E$.

6. (a) Bomb calorimeter is commonly used to find the heat of combustion of organic substances which consists of a sealed combustion chamber, called a bomb. If a process is run in a sealed container then no expansion or compression is allowed, so $w = 0$ and $\Delta U = q$.

$\Delta U < 0$, $w = 0$

9. (b) $\Delta H = \Delta E + \Delta nRT$

Since $\Delta n = -2$

Than $\Delta H = \Delta E - 2RT$.

10. (d) If $\Delta n = -ve$ than $\Delta H < \Delta E$.

12. (c) Hess's law is an application of first law of thermodynamics .

13. (c) At constant P or T

$\Delta H = \Delta U + \Delta nRT \Rightarrow$

$\Delta n = n_p - n_R = 2 - 4 = -2$

$\therefore \ \Delta H < \Delta U$.

16. (b) It is a combustion reaction, $\Delta H = -ve$.

17. (c) During isothermal expansion of ideal gas, $\Delta T = 0$

$\Delta H = \Delta E + P\Delta V = \Delta E + nR\Delta T = 0 + 0 = 0$.

18. (b) $W = 2.303\, nRT \log \frac{V_2}{V_1}$

$= 2.303 \times 1 \times 8.314 \times 10^7 \times 298 \log \frac{20}{10}$

$= 298 \times 10^7 \times 8.314 \times 2.303 \log 2$.

20. (a) The enthalpies of all elements in their standard state at $25^\circ C$ or 298K are zero.

21. (c) $\Delta E_V = E_P - E_R$.

22. (c) $\Delta E = q + w$.

23. (a) ΔE = 0 for reversible isothermal process.

25. (b) Hess law includes initial reactants and final products.

26. (a) At constant T and P internal energy of ideal gas remains unaffected.

27. (a) ΔE increases with temperature.

28. (a) $\Delta H = \Delta E + W$ or $\Delta H = \Delta E + P\Delta V$.

29. (bc) Heat of neutralisation of a strong acid and strong base is equal to $-13.7\, kcal$.

30. (c) $-W = +2.303 nRT \log \frac{p_1}{p_2}$

$$-W = 2.303 \times 1 \times 2 \times 300 \log \frac{10}{1}$$

$= 1381.8\, cal.$

31. (b) Joule-Thomson expansion is isoenthalpic.

32. (c) Here $\Delta n = 0$ so, $\Delta E = \Delta H$.

33. (b) $q = \Delta E - W$ if $q = 0$ for adiabatic process, than $\Delta E = W$.

34. (a) For this reaction $\Delta n = 0$ than $\Delta E = \Delta H$.

35. (c) As the system is closed and insulated no heat enter or leave the system, *i.e.* $q = 0$;
$\therefore \Delta E = Q + W = W$.

37. (c) $\Delta H - \Delta E = \Delta nRT$; $\Delta n = -3$
so, $\Delta H - \Delta E = -3RT$.

38. (b) According to Hess's law. The heat of reaction depends upon initial and final conditions of reactants.

39. (d) $\Delta H - \Delta E = \Delta nRT$
also, $2NH_{3(g)} \rightarrow N_{2(g)} + 3H_{2(g)}$
$\Delta n = 2$.

40. (c) $\Delta n = 0$ for this reaction so, $\Delta E = \Delta H$.

41. (d) $W = 0$ is not true.

42. (a) $W = 2.303nRT \log \frac{P_2}{P_1}$

$$= 2.303 \times 1 \times 2 \times 300 \log \frac{10}{2} = 965.84$$

at constant temperature, $\Delta E = 0$.
$\Delta E = q + w$; $q = -w = -965.84\, cal$.

43. (c) $q = 40J$
$w = -8J$ (work done by the system)
$\Delta E = q + w = 40 - 8 = 32J$.

44. (a) We know that $\Delta E = Q + W = 600 + (-300)$
$= 300J$
$W = 300$, because the work done by the system.

45. (c) Given that
$P_1 = 10\, atm$, $P_2 = 1\, atm$, $T = 300K$, $n = 1$
$R = 8.314 J/K/mol$
Now, by using

$$W = 2.303nRT \log_{10} \frac{P_2}{P_1}$$

$$= 2.303 \times 1 \times 8.314 \times 300 \log_{10} \frac{1}{10}$$

$W = 5744.1\, Joule$

46. (c) We know that internal energy of a gas depends upon its pressure and temperature. Thus if a gas expands at constant temperature and pressure, then its internal energy remains same.

47. (b) $PCl_5(g) \rightarrow PCl_3(g) + Cl_2(g)$
For this reaction $\Delta ng = 2 - 1 = 1$
Δng is positive, *i.e.,* there is an increase in the number of gaseous moles then $\Delta H > \Delta E$

48. (c) Enthalpy (H) is defined as the sum of internal energy $E + PV$, $H = E + PV$.

49. (d)
$(CH_3)_2C = CH_2(g) + 6O_2(g) \rightarrow 4CO_2(g) + 4H_2O(l)$
$\Delta ng = 4 - 6 = -2$ (i.e., negative)
we know that $\Delta H = \Delta E + \Delta ngRT$
$= \Delta E - (\Delta ng)RT$ $(\because \Delta ng = -ve)$
$\therefore \Delta H < \Delta E$

50. (b) Given number of moles =1
Initial temperature $= 27^o C = 300K$
Work done by the system $= 3\, KJ = 3000K$
It will be $(-)$ because work is done by the system.
Heat capacity at constant volume $(Cv) = 20J/k$
We know that work done
$W = -nC_V (T_2 - T_1)$;
$3000 = -1 \times 20\, (T_2 - 300)$
$3000 = -20T_2 + 6000$
$20T_2 = 3000$; $T_2 = \frac{3000}{20} = 150K$

51. (a) Internal energy of a system is a state function and extensive property and is independent of the path by which it is obtained.

52. (d) $N_2O_4(g) \rightarrow 2NO_2(g)$
For this reaction $\Delta ng = 2 - 1 = 1$
Δng is positive *i.e.,* there is an increase in the number of gaseous moles then $\Delta H > \Delta E$

53. (b) $2C + O_2 \rightarrow 2CO$; $\Delta H = -220\, KJ$
This reaction does not represent complete combustion of carbon, hence heat of combustion of carbon will not be equal to $110kJ$. The negative sign of ΔH indicates that this reaction is exothermic. Also, despite being spontaneous reaction, it requires initiation.

54. (c) $W = -P\Delta V = -1 \times 10^5 (1 \times 10^{-2} - 1 \times 10^{-3})$
$= -1 \times 10^5 \times 9 \times 10^{-3} = -900J$

55. (a) The exact value of internal energy is not known as it includes all type of energies of molecules constituting the given mass of matter such as translational, vibrational, rotational. The kinetic & potential energy of the nuclei & electron with in the individual molecules and the manner in which the molecule are linked together etc.
$E = E_{translational} + E_{rotational} + E_{vibrational}$
Thus, we can say that internal energy is partly potential and partly kinetic.

56. (b) $N_2(g) + O_2(g) \rightarrow 2NO(g)$; $\Delta n_g = 2 - 2 = 0$

$\Delta H = \Delta E + \Delta n_g RT$; $\Delta H = \Delta E + 0$; $\Delta H = \Delta E$

57. (d) $W = -p\Delta V$; $W = -3 \times (6 - 4)$

$W = -6 \times 101.32$ ($\therefore 1\ L\ atm = 101.32 J$)

$W = -608 J$

58. (d) $A(s) + 3B(g) \rightarrow 4C(s) + D(l)$

$\Delta ng = 0 - 3 = -3$; $\Delta H = \Delta E + \Delta ngRT$

$[\because \Delta E = \Delta U]$

$\therefore \Delta H = \Delta U + (-3)(RT)$

$\Delta H = \Delta U - 3(RT)$; $\Delta H = \Delta U - 3RT$

IInd & IIIrd Law of thermodynamics and Entropy

2. (d) When $\Delta S = +ve$ the change is spontaneous.

3. (d) Heat is always flow from the higher to lower temperature.

4. (b) Mixing of non-reacting gases increases randomness and so increase entropy .

5. (b) Entropy of the system increases as the process occur irreversibly and isothermally in an isolated system.

6. (d) $\Delta S^o = 2S^o_{HCl} - (S^o_{H_2} + S^o_{Cl_2})$

$= 2 \times 186.7 - (130.6 + 223.0) = 19.8 JK^{-1} mo$

9. (b) For adiabatic expansion $q = 0$ than according to following relation $\Delta S = \frac{q}{T}, \Delta S = 0$.

10. (c) It is the third law of thermodynamics.

11. (c) Entropy of gases is highest.

12. (c) $\Delta G = \Delta H - T\Delta S$

for spontaneous process ΔG *should be negative in option (3)* $\Delta H = -ve$ and $\Delta S = +ve$ *than*

$\Delta G = (-ve) - T(+ve) = -ve$

15. (c) For reverse reaction sign will be change.

16. (b) Solid $\rightarrow$ Gas, ΔS is maximum.

17. (d) $+ ve\ \Delta H$ and $- ve\ \Delta S$ both oppose the reaction.

18. (a) $\Delta S_{vap} = 186.5 / 373 = 0.5\ JK^{-1}\ mol^{-1}$.

20. (a) When ΔH = –*ve*, ΔS = +*ve* and ΔG = –*ve* than reaction is spontaneous .

21. (d) For endothermic process ΔS increases.

22. (c) Calculation of change in entropy is done at constant temperature and pressure both.

23. (a) When the value of entropy is greater, then ability of work is maximum.

24. (d) At equilibrium, ΔG = 0

Hence 0 = $\Delta H - T\Delta S$ or $\Delta H = T\Delta S$.

25. (c) $\Delta S_{vap} = \frac{\Delta H_{vap}}{T} = \frac{37.3\ KJ\ mol^{-1}}{373\ K}$

$= 0.1\ kJ\ mol^{-1}\ K^{-1} = 100\ J\ mol^{-1}\ K^{-1}$.

26. (d) Solid $\rightarrow$ Liquid, ΔS increases .

27. (c) $\Delta S = +ve$ than process is spontaneous.

28. (b) $\Delta S = +ve$ than the system is more disordered.

29. (c) Because solid $\rightarrow$ solid, ΔS is same and ΔH is –*ve*.

30. (b) $\Delta S_{vap} = \frac{\Delta H_{vap}}{T} = \frac{386}{298} = 1.2 kJ$.

31. (b) Processes (a) and (c) take place with the increase of no. of moles of gaseous species and hence the disorder or entropy increases. (b) on increasing pressure, disorder or randomness decreases and so also the entropy (d) is endothermic process and ΔS is positive.

32. (d) This is the statement of third law of thermodynamics.

33. (d) For isothermal expansion of ideal gas, $\Delta E = 0$.

34. (a) $\Delta S_{vap} = \frac{(900 \times 18)}{373} = 43.4\ JK^{-1}\ mol^{-1}$.

35. (c) Entropy of the mixture increases due to increase in impurity.

37. (c) If $\Delta H = +ve$ and $\Delta S = -ve$ than the reaction is non-spontaneous *i.e.* can not occur.

38. (a) $T_2 = 150 + 273 = 423K$

$T_1 = 25 + 273 = 298K$

$Q = 500K$

$\frac{W}{Q} = \frac{T_2 - T_1}{T_2}$;

$W = 500\left(\frac{423 - 298}{423}\right) = 147.7J$.

39. (c) According to III law of thermodynamics.

40. (c) When $\Delta H = +ve$ and $\Delta S = -ve$ reaction is non-spontaneous.

41. (c) $T_m = \frac{\Delta H_{fusion}}{\Delta S_{fusion}} = \frac{9.2}{0.008} = 1150K$.

42. (c) Here: Change in

Volume $(V) = 500 - 300 = 200cc = 0.2 litre$,

Pressure $(P) = 0.6 atm$ and heat liberated (q) = 10*J*

Work done

$(W) = P\Delta V = (0.2 \times 0.6) = 0.12 litre - atm$

But $1 litre - atm = 101.3 J$.

hence $W = 0.12 \times 101.3 = 12.156 J$. We also know that heat is liberated, therefore it would be negative. Thus change in $\Delta E = q + W = -10 + 12.16 = 2.16 J$.

43. (c) Formation of CO_2 is,

$C_{(s)} + O_{2(g)} \rightarrow CO_{2(g)}$

$\Delta S^o = 213.5 - 5.690 - 205 = 2.81\ JK^{-1}$.

45. (b) $H_2O_{(g)} \rightleftharpoons H_2O_{(l)}$

we know $\Delta G = \Delta H - T\Delta S$

at equilibrium $\Delta G = 0$

Therefore $\Delta H = T\Delta S$.

46. (a) We know that work done, $W = C_v(T_1 - T_2)$

$3 \times 1000 = 20(300 - T_2)$;

$\therefore 3000 = 6000 - 20T_2$

$\therefore T_2 = \frac{3000}{20} = 150K$.

48. (d) It does not violates the first law of thermodynamics but violates the II law of thermodynamics.

49. (d) $C_v = \frac{3}{2}RT$; $C_p = \frac{5}{2}RT$ for monoatomic gas

$C_v = \frac{5}{2}RT$; $C_p = \frac{7}{2}RT$ for diatomic gas

Thus for mixture of 1 *mole* each,

$C_v = \frac{\frac{3}{2}RT + \frac{5}{2}RT}{2}$ and $C_p = \frac{\frac{5}{2}RT + \frac{7}{2}RT}{2}$

Therefore, $C_p / C_v = \frac{3RT}{2RT} = 1.5$.

51. (c) $\Delta S = \frac{q_{rev}}{T}$ $\therefore$ unit of *S* is $JK^{-1}mol^{-1}$.

52. (b) $H_2O_{(l)} \rightleftharpoons H_2O_{(g)}$, $\Delta S = \frac{\Delta H_{vap}}{T}$,

$\Delta H_{vap.} = 2.257\ KJ\ /g$

or

$\Delta H_{vap} = 2.257 \times 18\ kJ\ /mol. = 40.7\ KJ\ /mol$

hence, $\Delta S = \frac{40.7}{373} = 0.109\ kJ/mol/K$.

53. (a) Liquid → Vapour, entropy increases.

54. (c) $NaNO_3$ is a solid, which is converted to liquid ions.

55. (c) Heat capacity of water per gram $= \frac{75}{18} = 4.17J$

$Q = mst$; $1000 = 100 \times 4.17 \times t$

$t = \frac{1000}{100 \times 4.17} = 2.4K$.

56. (c) As the work is done on system, it will be positive *i.e.* $W = +462\ joule$, $E = -128\ joule$ (heat is evolving)

From the Ist law of thermodynamics

$\Delta E = q + w = (-128) + (+462) = +334\ Joules$.

57. (a) Gases show highest entropy.

58. (b)

$$\begin{array}{lccc} & H^+_{(aq)} + & OH^-_{(aq)} \rightarrow & H_2O_{(l)} \\ S^o(298K)K^{-1}mol^{-1} & & -10.7 & +70 \end{array}$$

$\Delta S^o(298K) = \Delta S_P - \Delta S_R = 70 - (-10.7 + 0)$

$80.7\ JK^{-1}mol^{-1}$

59. (d) The entropy change $= \frac{\text{heat of vaporisation}}{\text{temperature}}$

Here, heat of vaporisation $= 540\ cal/gm$

$= 540 \times 18\ cal\,mol^{-1}$

Temperature of water $= 100 + 273 = 373K$

$\therefore$ entropy change

$= \frac{540 \times 18}{373} = 26.06\ cal\,mol^{-1}K^{-1}$

60. (b) Given that, $T_1 = 500K$, $T_2 = 300K$

By using, $\eta = \frac{T_1 - T_2}{T_1}$

$= \frac{500 - 300}{500} = \frac{200}{500} = 0.4$.

61. (b) It is molar heat capacity.

62. (d) Entropy is the measure of randomness in the molecules. Randomness is maximum in case of gases. Hence, entropy is maximum for water vapours.

63. (a) Standard entropy of formation of $CO_2(g)$ = standard entropy of $CO_2(g)$ − [Standard entropy of $C(s)$ − standard entropy of $O_2(g)$]

$= 213.5 - [5.740 + 205] = 2.76\ J\ /K$.

64. (c) Third law of thermodynamics help in calculating entropy of different temperatures.

65. (a) In case of gas randomness is maximum therefore entropy is maximum in case of steam.

66. (c) $\Delta S_{system} + \Delta S_{surroundings} > O$ (for spontaneity)

Because of $\Delta S = R \ln \frac{V_2}{V_1}$

Here the volume of gas increase from V_1 to V_2 at constant temperature T.

The total increase in entropy of the system and its surrounding during the spontaneous process of expansion considered above is, thus $R \ln\left(\frac{V_2}{V_1}\right)$

since $V_2 > V_1$ it is obvious that the spontaneous (irreversible) isothermal expansion of a gas is accompanied by an increase in the entropy of the system and its surrounding considered together.

$\Delta S_{system} + \Delta S_{surroundings} > 0$.

67. (b) $\Delta G = \Delta H - T\Delta S$

at constant temperature and pressure $\Delta G = 0$

$0 = \Delta T - T\Delta S$ so $\Delta H = T\Delta S$

68. (b) $dS = \frac{dQ_{rev.}}{T}$; $T = \frac{30 \times 10^3}{75}$; $T = 400K$

Heat of reaction

1. (b) $C + O_2 \rightarrow CO_2 + 94.2\ Kcal.$ .....(i)

$$H_2 + \frac{1}{2}O_2 \rightarrow H_2O + 68.3\ Kcal. \quad ....(ii)$$

On multiplication of *eq*. (ii) by 2 and than adding in *eq*. (i)

$C + 2H_2 + 2O_2 \rightarrow CO_2 + 2H_2O + 230.8\ Kcal$ ...(iii)

On subtracting *eq*. (iii) by following *eq*.

$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O + 210.8\ Kcal.$ we get,

$C + 2H_2 \rightarrow CH_4\ \Delta H = 20\ Kcal.$

2. (b) $\Delta S = 16J\ mole^{-1} K^{-1}$

$$T_{b.p.} = \frac{\Delta H_{vapour}}{\Delta S_{vapour}} = \frac{6 \times 1000}{16} = 375K$$

4. (d) Heat of neutralisation between strong acid and a strong base is about $-13.7\ Kcal.$

6. (b) Effect of temperature in heat of reaction is given by Kirchoff's equation.

7. (c) Heat of neutralisation between strong acid and a strong base is about $-13.7\ Kcal.$

8. (a) For exothermic reactions $H_p < H_R$.

For endothermic reactions $H_p > H_R$.

9. (b) 78*g* of benzene on combustion produces heat = – 3264.6 *kJ*

$\therefore 39g$ will produce $= \frac{-3264.6}{2} = -1632.3\,kJ$.

10. (a) *eq*. (i) + *eq.* (ii) gives the required result.

11. (bcd) (b,c,d) are endothermic reactions because they proceeds by the absorption of heat.

12. (a) Change of liquid to vapour takes energy in the form of heat so it is endothermic reaction.

13. (d) In exothermic reactions heat is evolute.

15. (c) $\Delta H = -ve$ for exothermic reaction.

$\Delta H = +ve$ for endothermic reaction

Enthalpy of fusion is + *ve.*

16. (a) Heat of neutralisation will be less than $-57.33\ kJ\ /mole$ because some amount of this energy will be required for the dissociation of weak base (MgO)

18. (a) $H_2 + O_2 \rightarrow H_2O_2\quad \Delta H_f^o = -188kJ\ /mole$ ....(i)

$$H_2 + \frac{1}{2}O_2 \rightarrow H_2O\quad \Delta H_f^o = -286kJ\ /mole \quad ....(ii)$$

eq. (i) – eq. (ii) × 2 gives the required result.

19. (b) Graphite $\rightarrow$ diamond $\Delta H_t = (x - y)kJ\ mol^{-1}$.

21. (c) Heats of combustions are always exothermic except oxidation of *N* as,

$$N_2 + \frac{1}{2}O_2 \rightarrow N_2O\quad \Delta H = +ve$$

$$N_2 + O_2 \rightarrow 2NO\quad \Delta H = +ve$$

22. (a) For exothermic reactions $H_p < H_R$.

For endothermic reactions $H_p > H_R$.

23. (d) Aim: $2C + H_{2(g)} \rightarrow C_2H_{2(g)}$.

eq. (ii) + eq. (iii) → eq. (iv) – eq. (i)

find the required result.

24. (c) Enthalpy of formation of *HCl.*

25. (c) Heat of neutralisation between strong acid and a strong base is about $-13.7\ Kcal.$

26. (b) For endothermic reaction, $\Delta H = +ve$.

27. (b) Heat of neutralisation is less than 56.1 *Kcal* when a strong base and a weak acid reacts.

28. (b) Aim: $CO + \frac{1}{2}O_2 \rightarrow CO_2$

$$\Delta H = \Delta H_f^0(CO_2) - \left[\Delta H_f^0(CO) + \frac{1}{2}\Delta H_f^0(O_2)\right]$$

$$= -94.0 - (-26.4) = -67.6\ kcal.$$

29. (a)

(i) $H_2 + \frac{1}{2}O_2 \rightarrow H_2O,\ \Delta H = -241kJ$

(ii) $C_6H_{10} + \frac{17}{2}O_2 \rightarrow 6CO_2 + 5H_2O, \Delta H = -3800kJ$

(iii) $C_6H_{12} + 9O_2 \rightarrow 6CO_2 + 6H_2O,\ \Delta H = -3920kJ$

$C_6H_{10} + H_2 \rightarrow C_6H_{12}$

Eq. (i) + Eq. (ii) – Eq. (iii)

$$\Delta H = -241 - 3800 - (-3920)$$

$$= -4041 + 3920 = -121kJ$$

30. (c) NH_4OH is a weak base. Heat of neutralisation < 13.7*kcal.*

31. (a) CH_4 is the best fuel because its calorific value $= \frac{-212.8}{16} = -13.3 kcal/g$ is higher among the other gases.

32. (a) Find ΔH for $CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O_{(g)}$.

34. (b) In neutralisation of a strong acid and base only H^+ and OH^- ions react.

35. (b) When both acid and base are strong than heat of neutralisation is $57.1 kJ\ mol^{-1}$.

36. (a) $C_2H_6 + \frac{7}{2}O_2 \rightarrow 2CO_2 + 3H_2O$ substitute the values.

37. (a) Decomposition is an endothermic process.

38. (d) ΔH for this reaction is Heat of reaction.

40. (b) One mole of H_2O is formed from its initial components.

41. (c) One mole of a substance is completely oxidized in air.

42. (c) *S* (rhombic) $+ O_2 \rightarrow SO_2$, $\Delta H = 70960 cal.$ ...(i)

S (monoclinic) $+ O_2 \rightarrow SO_2$ $\Delta H = 71030 cal$ ...(ii)

Aim: S (rhombic) → *S* (monoclinic)

eq. (i) – *eq*. (ii) gives the required result.

43. (b) When $H_2O_{(l)}$ is convert to form $H_2O_{(g)}$, heat is absorbed hence $\Delta H_1 > \Delta H_2$.

44. (b) Out of given substances, kerosene oil has maximum calorific value.

45. (b) $C_{(S)} + O_{2(g)} \rightarrow CO_{2(g)}$, $\Delta n_g = 1 - 1 = 0$

$\therefore \Delta E = \Delta H = -94\ kcal$

$\Delta E = E_{CO_2} - (E_C + E_{O_2}) = E_{CO_2} - (0 + 0)$

or $E_{CO_2} = \Delta E = -94\ kcal.$

46. (b) 0.2 *mole* will neutralize 0.2 mole of HNO_3, heat evolved $= 57 \times 0.2 = 11.4 kJ$.

47. (a) Suppose heat evolved in I^st^ case is Q_1 and that in the II^nd^ case it is Q_2. Then $Q_2 = \frac{1}{2}Q_1$.

But $Q_1 = 1000T_1$ and $Q_2 = 500T_2$

$\therefore 500\ T_2 = \frac{1}{2} \times 1000\ T_1$ $i.e. T_2 = T_1$.

48. (c) Enthalpy of a compound = Heat of reaction of that compound.

49. (e) It is the definition of heat of neutralization.

50. (b) $\Delta H = -ve$ for exothermic compound.

51. (a) If acid or base or both are strong, heat of neutralization $= 13.7\ kcal.$

52. (b) Both NH_4OH and CH_3COOH are weak.

53. (c) $57.1 \times 0.25 = 14.3\ kJ\ mol^{-1}$.

54. (c) Heat of formation is for 1 *mole.*

Hence $\Delta H_f^0(HI) = -12.40/2 = -6.20 kcal.$

55. (b) Chemical dissociations are reversible and endothermic.

57. (c) Given,

(i) $CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$, $\Delta H = +20\ kcal$

(ii) $C + O_2 \rightarrow CO_2$, $\Delta H = -40\ kcal.$

(iii) $H_2 + \frac{1}{2}O_2 \rightarrow H_2O$, $\Delta H = -10\ kcal.$

Aim: $C + 2H_2 \rightarrow CH_4$

(ii) + 2 × (iii) – (i) gives.

$\Delta H = -40 + 2(-10) - (+20) = -80\ kcal.$

58. (d) For exothermic reaction heat is evolved.

59. (c) $H_2O_{(l)} \xrightarrow{\text{electrolysis}} H_{2(g)} + \frac{1}{2}O_{2(g)}$.

61. (d) All other are combustion phenomena.

62. (c) $\Delta H_{\text{combustion}}$ = –*ve*, so exothermic process.

63. (b) Aim: $K_{(S)} + \frac{1}{2}O_{2(g)} + \frac{1}{2}H_{2(g)} \rightarrow KOH_{(S)}$

eq. (ii) + *eq*. (i) – *eq*. (iii) gives

$\Delta H = -48 + (-68.39) - (-14)$

$= -68.39 - 48 + 14$.

64. (a) By definition of heat of formation.

68. (c) $C_D \rightarrow C_G, \Delta H = -453.5\ cal.$

i.e. energy of C_G is less and thus more stable.

69. (a) $\Delta H_{\text{combustion}}$ is always negative .

70. (d) $\Delta H_{\text{reaction}} = \Delta H_f^0(N_2O_4) - 2\Delta H_f^0(NO_2)$

$= 2 - 2(8) = -14\ kcal.$

71. (a) $\Delta H - \Delta E = \Delta nRT = 3 \times 8.314 \times 298$

$= -7432\ J = -7.43 kJ$.

72. (b) Aim: $C_{(\text{graphite})} \rightarrow C_{(\text{diamond})}$; *eq*. (i) – (ii) gives the result.

73. (d) In the formation of a compound, more the heat absorbed, less stable is the compound.

74. (c) $C_{(\text{graphite})} + 2H_{2(g)} = CH_{4(g)}$.

75. (b) Heat of formation is the formation of one mole of the substance from its elements.

76. (b) $\Delta H_{(\text{reaction})} = 2\Delta H_f^0(MgO) = -\Delta H_f^0(SiO_2)$

$= 2(-34.7) - (-48.4) = -21 kJ$.

77. (a) *eq*. (i) + *eq*. (ii) + *eq*. (iii) gives

$X = 131 - 282 - 242 = -393 kJ$.

78. (d) It is the definition of heat of transition.

79. (d) $C_{(\text{graphite})} \rightarrow C_{(\text{diamond})}, \Delta H = 1.9 kJ$

$C_{(\text{graphite})} + O_2 \rightarrow CO_2, \Delta H = -\Delta H_1$

$C_{(\text{diamond})} + O_2 \rightarrow CO_2, \Delta H = -\Delta H_2$

$(-\Delta H_1)-(-\Delta H_2)=1.9\,kJ$ or $\Delta H_2=\Delta H_1+1.9$

For combustion of $6g, \Delta H_2>\Delta H_1$ by $1.9/2=0.95\,kJ$.

80. (a) $H_{\text{product}} \times H_{\text{reactant}}$ for exothermic reaction.

81. (b) Due to high electron affinity of *Cl* the highest energy is evolved.

82. (b) $CH_4+2O_2\rightarrow CO_2+2H_2O$

Molecular weight of $CH_4=12+4=16$

∴ On the combustion of 2.0*gm* of methane= 25.0 *kcal*

∴ On the combustion of $16.0gm=\frac{25\times16}{2}=200\,kcal.$

83. (a) $CH_4+2O_2\rightarrow CO_2+2H_2O$.

84. (b) $C_2H_4+3O_2\rightarrow 2CO_2+2H_2O$

$\Delta H_{\text{reaction}}=[2\times\Delta H_f^o(CO_2)+2\times\Delta H_f^o(H_2O)]$

$-[\Delta H_f^o(C_2H_4)+3\times\Delta H_f^o(O_2)]$

$=[2(-394)+2(-286)]-[52+0]=-1412\,kJ$

.

85. (b) $C+O_2\rightarrow CO_2+394\,kJ$.

$2C+2O_2\rightarrow 2CO_2+788\,kJ$ ....(i)

$2CO+O_2\rightarrow 2CO_2+569\,kJ$ ....(ii)

$2CO_2\rightarrow 2CO+O_2-569\,kJ$ .....(iii)

eq. (i) + *eq*. (iii) = –109.5 *kJ mol*$^{-1}$.

86. (c) $\Delta H_f=\frac{44}{2}kcal=22\,kcal$.

87. (a) $CaO_{(s)}+H_2O_{(l)}\rightarrow Ca(OH)_2$ is exothermic.

88. (b) $\Delta H=-ve$ in exothermic reaction.

89. (d) According to the definition of heat of formation.

90. (d) Multiplying *eq*. (ii) by (iii) and *eq*. (iii) by (vi), and then add

$6C+3H_2+\frac{15}{2}O_2\rightarrow$

$6CO_2+6H_2O;\ \Delta H=3218.7$

Subtract *eq*. (i) from the above equation and find the required result.

91. (a) *HF* is more stable than HCl.

92. (c) $\Delta H(H_P-H_R)=q_p$.

93. (b) $\Delta H=+ve$ for endothermic reaction.

94. (a) $\Delta H=\frac{13.95\times44}{2.2016}=278.7\,kcal$.

95. (d) *eq*. (i) + *eq*. (ii) gives the required result.

96. (d) Standard molar heat enthalpy (H^o) of a compound is equal to its standard heat of formation from most stable states of initial components.

97. (c) In the complete combustion of butanol $\Delta H>\Delta E$.

98. (a) *X* – *Y* and find the required result.

99. (c) $S+O_2\rightarrow SO_2\quad \Delta H=-298.2\,kJ$ ....(i)

$SO_2+\frac{1}{2}O_2\rightarrow SO_3\quad \Delta H=-98.2\,kJ$ ....(ii)

eq. (i) – (ii) and find the required result.

100. (c) $C+2S\rightarrow CS_2\quad \Delta H=?$

$C+O_2\rightarrow CO_2\quad \Delta H=-393.3\,kJ$ ....(i)

$S+O_2\rightarrow SO_2\quad \Delta H=-293.72\,kJ$ .....(ii)

$CS_2+3O_2\rightarrow CO_2+2SO_2\quad \Delta H=-1108.76\,kJ$ ..... (iii)

eq. (ii) × 2 + *eq*. (i) – (iv) *eq*. (iii) – *eq*. (iv) and find required result .

101. (b) Fermentation is exothermic reaction.

102. (c) $CH_4+2O_2\rightarrow CO_2+2H_2O$.

103. (d) Use $\Delta H=\Delta E+\Delta nRT$

$\Delta H=19+2\times2\times10^{-3}\times300=20.2\,kcal$; $\Delta n=2$.

104. (d) $-20.6-8.8\,KJ\ mol^{-1}=-29.4\ kJ$.

106. (a) Subtract equation (ii) from (i).

107. (c)

$CH_4+2O_2\rightarrow CO_2+2H_2O, \Delta H=-890.4\,kJ$ ....(i)

$C+O_2\rightarrow CO_2,\ \Delta H=-395.5\,kJ$ .....(ii)

$C+O_2\rightarrow CO_2,\ \Delta H=-395.5\,kJ$ .....(ii)

$H_2+\frac{1}{2}O_2\rightarrow H_2O,\ \Delta H=-285.8\,kJ$ .....(iii)

from (i), (ii), (iii).

$\Delta H_{comb.}(CH_4)$

$=\Delta H_f(CO_2)+2\Delta H_f(H_2O)-\Delta H_f(CH_4)-2\Delta H_f(O_2)$

$=-890.4=-395.5+2(-285.5)-\Delta H_f(CH_4)-2\times0$

$\Delta H_f(CH_4)=-76.7\,kJ\ mol^{-1}$.

108. (d) As methanoic acid is weak acid, heat of neutralization < *x*.

109. (d) Neutralization of a strong acid by a strong base is always same.

110. (c) $S + O_2 \rightarrow SO_2, \ \Delta H_f = -4.6 kJ$

∵ 0.5 *gm.* of sulphur on burning produce 1*gm* of SO_2

∴ 32 *gm* of sulphur on burning produce 64 *gm.*. of SO_2

$\therefore \Delta H = (-4.6 kJ) \times 64 = -294.4 kJ$.

111. (a) $3O_2 \rightleftharpoons 2O_3$ – energy is given out.

112. (b) $\Delta H \ per 1.6g = \frac{72 \times 1.6}{180} = 0.64 kcal$.

113. (a) $C + O_2 \rightarrow CO_2, \ \Delta H = -394 kJ$ .....(i)

$2H_2 + O_2 \rightarrow 2H_2O, \ \Delta H = -568 kJ$ ....(ii)

$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O, \ \Delta H = -892 kJ$ .....(iii)

(i) + (ii) – (iii) and find the required result.

115. (a) No doubt heat evolved during neutralisation of $250 cm^3$ of each acid and base is five time the heat evolved during neutralisation of $50 cm^3$ of each acid and base but the quantity if solution taking heat is also five time thus same temperature rise is noticed.

116. (a) $H_2 + \frac{1}{2}O_2 \rightarrow H_2O_{(l)}; \ \Delta H = -285.8 KJ$

$H_2O_{(l)} \rightarrow H_2O_{(g)}; \ \Delta H = 44 KJ$

$\therefore H_2 + \frac{1}{2}O_2 \rightarrow H_2O_{(g)}; \ \Delta H^o = -241.8 KJ$

117. (b) Given: Weight of iron burnt $= 4g$; Heat liberated $= 29.28 KJ$ and atomic weight of iron $(Fe) = 56$. We know that in ferric oxide (Fe_2O_3), $2 \ moles$ of iron or $2 \times 56 = 112 gram$ of iron are burnt. We also know that when $4 grams$ of iron are burnt, then heat liberated = 29.28 *kJ*, therefore when $112 grams$ of the iron are burnt, then heat liberated $= \frac{29.28 \times 112}{4} = -819.8 kJ$ (Minus sign due to liberation of heat).

118. (c) $H^+ + OH^- \rightarrow H_2O, \Delta H_{\text{neutralization}} = 13.7 kcal$.

119. (b) $\Delta H \ / mole$ of $FeS = \frac{3.77 \times 56}{2.1} = 100.5$.

120. (a) Heat of formation $= \frac{194}{2} = 97 kJ$.

121. (a) $\Delta H = \Delta H_{\text{ioniz}} + \Delta H_{neu}$ = $-50.6 = \Delta H_{\text{ioniz}} + (-55.9)$

$\Delta H_{\text{ioniz}} = +5.3 kJ \ / mol$.

122. (a) Strong acid (HNO_3) and strong base $(LiOH)$.

123. (d) $\Delta H = \Delta E + \Delta nRT$ or $\Delta E = \Delta H - \Delta nRT$

$\therefore \Delta E = +7.3 - \frac{1}{2} \times 0.002 \times 298$

$= 7.3 - 0.298$ = 7 *kcal*.

124. (b) Heat evolved during burning of $39g$

$C_6H_6 = \frac{781.0 \times 39}{78} = 390.5 kcal mol^{-1}$

125. (b) By (i) + (ii) ; $Na + \frac{1}{2}Cl_2 \rightarrow NaCl, \ \Delta H = -196 kcal$.

126. (b) $C + O_2 \rightarrow CO_{2(g)}, \ \Delta H_f^o = -393.5 kJ \ mol^{-1}$ ....(i)

$C + \frac{1}{2}O_2 \rightarrow CO_{(g)}, \ \Delta H_f^o = -110.5 kJ \ mol^{-1}$ ....(ii)

$H_2 + \frac{1}{2}O_2 \rightarrow H_2O_{(g)}, \ \Delta H_f^o = -241.8 kJmol^{-1}$ ...(iii)

By (ii) + (iii) – (i)

$CO_{2(g)} + H_{2(g)} \rightarrow CO_{(g)} + H_2O_{(g)}, \ \Delta H = +41.2$.

127. (c) More +*ve* is ΔH_s more is heat of solution.

128. (d) CS_2 is formed from its initial components carbon and sulphur so, ΔH is heat of formation of CS_2.

129. (d) $\Delta H = 18500 = \Delta E + \Delta nRT$

or $18500 = \Delta E + (-1) \times 2 \times 298 = 19096 cal$.

130. (b) Heat evolved during combustion of 0.39*g*

$C_6H_6 = \frac{3250 \times 0.39}{78} = 16.25 kJ$.

131. (d) By (i) – (ii) : $C + \frac{1}{2}O_2 \rightarrow CO; \ \Delta H = -229.2$.

132. (b) Strong acid (HCl) and strong base $(NaOH)$ shows $\Delta H_{\text{neutralization}}$ = –57.3 *kJ*.

133. (d) By (i) – (ii) and find required result.

134. (a) $CO_{(g)} + \frac{1}{2}O_{2(g)} \rightarrow CO_{(g)}, \Delta n = 1 - 1 + \frac{1}{2} = -\frac{1}{2}$

$\Delta H = \Delta E + \Delta nRT$

$$\Delta H = -283.3 - \frac{1}{2}\times\frac{8.314}{1000}\times 290 = -284.5kJ\ .$$

135. (a) $H_2 + \frac{1}{2}O_2 \rightarrow H_2O \quad \Delta H = -188kJ/mole$ ....(i)

$H_2 + O_2 \rightarrow H_2O_2; \quad \Delta H = -286kJ/mole$ ......(ii)

By 2 × (i) and (ii)

$2H_2 + O_2 \rightarrow 2H_2O; \ \Delta H = -376kJ/mole$ ..... (iii)

$2H_2 + 2O_2 \rightarrow 2H_2O_2 \quad \Delta H = -572kJ/mole$ .....(iv)

By (iii) – (iv)

$2H_2O_2 \rightarrow 2H_2O + O_2 \quad \Delta H = +196kJ$.

136. (a) ΔH for $C_2H_6 = -341.1\,K\,cal$

its calorific value $= \frac{-341.1}{30} = -11.37\,kcal/g$.

ΔH for $C_2H_2 = -310.0\,kcal$

its Calorific value $= \frac{-310.0}{26} = -11.92$,

hence C_2H_2 is a better fuel.

138. (c) For the decomposition of 9*gm* of water heat required $= 142.5\,kJ$

we know $H_2O = 2 + 16 = 18$

Therefore heat required for decomposition of 18*gm* water $= \frac{18}{9}\times 142.5 = 285\,KJ$

Than, enthalpy of formation of water is reverse of heat required = – 285 *kJ*.

139. (d) $C_6H_{6(g)} + \frac{15}{2}O_{2(g)} \rightarrow 6CO_{2(g)} + 3H_2O_{(g)}$

$\Delta n = 6 + 3 - 1 - \frac{15}{2} = +\frac{1}{2}$.

140. (b) By 2 × (i) + (ii) – (iii)

ΔH of methane $= 20.0\,kcal$.

141. (c) Heat of neutralization of strong acid and weak base is less than $13.7\,kcal\,mol^{-1}$.

142. (d) $\Delta E = 0$ for a cyclic process.

143. (c) $22.0 \times 2 = 44\,kcal$.

144. (b) 0.3 mole OH^-, neutralize 0.3 mole of HNO_3

Evolved heat, $= 57.1 \times 0.3 = 17.13kJ$

146. (d) Compounds with high heat of formation are less stable because energy rich state leads to instability.

147. (b) CH_4 required $= \frac{445.15\times 16}{890.3} = 8gm$.

148. (c) $C_{(s)} + 2H_{2(g)} \rightarrow CH_{4(g)}$ .....(i)

$C_{(s)} + O_{2(g)} \rightarrow CO_{2(g)} \quad \Delta H = -94\,kcal\,mol^{-1}$ .....(ii)

$H_{2(g)} + \frac{1}{2}O_{2(g)} \rightarrow H_2O_{(l)} \quad \Delta H = -68\,kcal\,mol^{-1}$ ... (iii)

$CH_4 + 3/_2\,O_2 \rightarrow CO_2 + 2H_2O$

$\Delta H = -213\,kcal\,mol^{-1}$ ... (iv)

to obtain equation (i) operate-(ii) + 2 × (iii) – (iv).

149. (b) $\Delta H = +ve$ for endothermic reactions.

150. (b) It pertains to neutralization of strong acid weak base.

151. (d) Strong base (*KOH*) and strong acid (*HCl*)

153. (b) This reaction absorbed heat, so it is endothermic reaction.

154. (b) $C + O_2 \rightarrow CO_2, \ \Delta H = -94.3$

This is also heat of formation of CO_2

$C + \frac{1}{2}O_2 \rightarrow CO, \ \Delta H = -26.0$.

155. (b) $X = \frac{1}{2}Y$.

157. (a) Molecular weight of $NH_4NO_3 = 80$

Heat evolved $= 1.23 \times 6.12$

$\therefore$ Molar heat capacity $= 1.23 \times 6.12 \times C$.

158. (d) Both X_e and F_2 are gaseous elements at 25^0C and in their standard states and form $XeF_{4(g)}$ hence $\Delta H^\circ_{(f)} = \Delta H^\circ_{\text{react}}$.

159. (c) According to Hess low, enthalpy change for a reaction does not depend on the nature of inter mediate reaction steps.

160. (d) By (ii) – (i), $C_{gr} \rightarrow C_{dia},\ \Delta H = +1.9$.

162. (c) Heat of neutralization of strong acid and strong base is equal to the $-57.32\,KJ\ mol^{-1}$

163. (c) $C + O_2 \rightarrow CO_2\ \Delta H = -393.5\,KJ\ /mol$

$\because$ $44\,gm$ of CO_2 form by which heat released $= -393.5\,kJ$

$\therefore$ $1 gm$ of CO_2 form by which heat released

$= -\dfrac{393.5}{44}$

$\therefore$ $35.2 gm$ (given) of CO_2 form by which heat released

$= -\dfrac{393.5}{44} \times 35.2 = -315 kJ$

164. (c) $C_{(graphite)} + 2H_2(g) \rightarrow CH_4(g)$

165. (c) Heat of formation of a substance is the heat exchanged when one mole of that substance is formed by its constituent elements.

$\because$ Heat evolved when 1 mole $(44g)\, CO_2$ is formed $= 393 kJ$

$\therefore$ Heat evolved when $0.156 Kg\, (156g)$ is formed $= \dfrac{393 \times 156}{44}$

$\therefore$ ΔH for the process $= 1572 kJ$ $= -1572.0 kJ$

166. (b) It is heat of neutralisation $(13.7 Kcal)$ for strong acid and strong base.

167. (d) $C(s) + O_2(g) \rightarrow CO_2(g)$

$\Delta H = -393.5 KJ\ mol^{-1}$ .....(i)

$CO(g) + 1/2 O_2(g) \rightarrow CO_2(g)$

$\Delta H = -283 KJ\ mol^{-1}$ .....(ii)

On substracting equation (ii) from equation (i)

We get

$C(s) + O_2(g) \rightarrow CO(g)$;

$\Delta H = -110.5 KJ\ mol^{-1}$

The enthalpy of formation of carbon monooxide per mole $= -110.5 KJ\ mol^{-1}$

168. (d) 1 mole (i.e.,) $16 gm$ of methane on combustion liberate $890 kJ$

$\therefore$ $3.2 gm$ will liberate $= \dfrac{890 \times 3.2}{16}$ $= 178 KJ$

169. (c) $C + O_2 \rightarrow CO_2$; $\Delta H = q$

$C + 1/2 O_2 \rightarrow CO$; $\Delta H = -12$ .....(i)

$CO + 1/2 O_2 \rightarrow CO_2$; $\Delta H = -10$ .....(ii)

adding equation (i) and (ii) we can get

$\Delta H = -12 + (-10) = -22$

170. (b) $C + O_2 \rightarrow CO_2$; $\Delta H_F = -490 KJ\ /mol$ – (I)

$H_2 + 1/2 O_2 \rightarrow H_2O$; $\Delta H_F = -240 KJ\ /mol$ – (II)

$8C + 18H \rightarrow C_8H_{18}$; $\Delta H_F = +160 KJ\ /mol$ – (III)

applying

(I) $\times 8 +$ (II) $\times 9 +$ (III)

$C_8H_{18} + \dfrac{25}{2} O_2 \rightarrow 8CO_2 + 9H_2O$

$\Delta H^o = -3920 - 2160 - 160 = 6240 KJ\ /mol$

$\Delta H^o =$ for 6 moles of octane $= 6240 \times 6$

$= 37440 KJ\ /mol = -37.4 KJ$

171. (d) $2Fe + \dfrac{3}{2} O_2 \rightarrow Fe_2O_3; \Delta H = -193.4 kJ$ .....(i)

$Mg + \dfrac{1}{2} O_2 \rightarrow MgO;\ \Delta H = -140.2 kJ$ .....(ii)

On multiplying eq. (ii) by 3

$3Mg + \dfrac{3}{2} O_2 \rightarrow 3MgO;\ \Delta H = -420.6 kJ$ .....(iiii)

Resulting equation can be obtained by subtracting eq. (i) from (iii)

$3Mg + \dfrac{3}{2} O_2 \rightarrow 3MgO;\ \Delta H = -420.6 kJ$

$2Fe + \dfrac{3}{2} O_2 \rightarrow Fe_2O_3;\ \Delta H = -193.4 kJ$

Subtraction :

$3Mg + Fe_2O_3 \rightarrow 2Fe + 3MgO; \Delta H = -227.2 kJ$

172. (c) HCl and KOH both are strong

Bond energy

1. (b) $XY \longrightarrow X_{(g)} + Y_{(g)}$; $\Delta H = +a\ kJ\ /mole$ ....(i)

$X_2 \longrightarrow 2X$; $\Delta H = +a\ kJ\ /mole$ .... (ii)

$Y_2 \longrightarrow 2Y$; $\Delta H = +0.5\, a\ kJ\ /mole$ ....(iii)

$\dfrac{1}{2} \times (ii) + \dfrac{1}{2} \times (iii) - (i)$, gives

$$\frac{1}{2}X_2 + \frac{1}{2}Y_2 \longrightarrow XY \;;$$

$$\Delta H = \left(+\frac{a}{2} + \frac{0.5}{2}a - a\right) kJ/mole$$

$$+\frac{a}{2} + \frac{0.5a}{2} - a = -200$$

$$a = 800$$

2. (a) $4g\,H_2 = 2$ *moles*. Bond energy for 1 *mole* of $H_2 = 208/2 = 104\ kcal.$

4. (d) By definition of Hess's law.

5. (c) Aim: $\frac{1}{2}H_2 + \frac{1}{2}Cl_2 \to HCl$

$$\Delta H = \sum B.E._{\text{(Products)}} - \sum B.E._{\text{(Reactants)}}$$

$$= B.E.(HCl) - \left[\frac{1}{2}B.E.(H_2) + \frac{1}{2}B.E.(Cl_2)\right]$$

$$= -103 - \left[\frac{1}{2}(-104) + \frac{1}{2}(-58)\right]$$

$$= -103 - (-52 - 29) = -22\ kcal.$$

6. (c) First ionization potential of $Li = 5.4eV$

Electron affinity of $Cl = 3.61eV$

We have $\Delta H = I.P. - E.A.$

$$= 5.4 - 3.61 = 1.80eV = 1.80 \times 1.6 \times 10^{-22} kJ$$

$$\Delta H = 2.86 \times 10^{-22} kJ\ ,$$

for 1*mol* Avogadro's number $= 6.02 \times 10^{23}$.

$$\Delta H = 2.86 \times 10^{-22} \times 6.02 \times 10^{23} = 170 kJ/mole.$$

7. (b) $\frac{-166}{4} = -41.5 kJ/mole$.

8. (d) $\frac{1}{2}H_2 + \frac{1}{2}Cl_2 \to HCl,\ \Delta H = -90 KJ$

$$\therefore \Delta H = \frac{1}{2}E_{H-H} + \frac{1}{2}E_{Cl-Cl}$$

$$\text{or } -90 = \frac{1}{2} \times 430 + \frac{1}{2} \times 240 - E_{HCl}$$

$$\therefore E_{H-Cl} = 425 kJ\ mol^{-1}.$$

9. (b) $CH_4 \to C + 4H,\ \Delta H = 320$

$E_{C-H} = 90 cal$

$C_2H_6 \to 2C + 6H,\ \Delta H = 360$

$\therefore 360 = E_{C-C} + 6E_{C-H}$

$\therefore E_{C-C} = 360 - 320 = 40\ cal.$

10. (b) $H-H + Br-Br \to 2H-Br$

$433 + 192 \qquad 2 \times 364$

$625 \qquad 728$

Energy absorbed = Energy released

Net energy released $= 728 - 625 = 103 kJ$

i.e., $= \Delta H = -103 KJ$

Free energy and Work function

1. (d) ΔG at equilibrium = 0.

2. (b) For spontaneous change $\Delta G = -ve$.

3. (a) When $\Delta G = -ve$ than the reaction is spontaneous in nature.

5. (acd)When $\Delta H = +ve$ and $\Delta S = -ve$ than the reaction is non-spontaneous.

7. (c) Because the reaction is spontaneous .

8. (c) $\Delta G = -ve.$

9. (a) $\Delta G_T = nRT \ln\frac{P_2}{P_1}$.

10. (a) $\Delta G = 0$ for equilibrium.

11. (d) At equilibrium $\Delta G = 0$.

12. (a) $\Delta G^o = -2.303RT \log K$

$$-4.606 = -2.303 \times 0.002 \times 500 \log K$$

$$\log K = 2,\ K = 100.$$

14. (d) Spontaneous change shows $\Delta G = -ve$.

15. (b) $\Delta G = \Delta H - T\Delta S,\ T = 25 + 273 = 298K$

$$= -11.7 \times 10^3 - 298 \times (-105) = 19590J = 19.59kJ$$

18. (c) If $\Delta G = -ve$ reaction is spontaneous.

20. (b) $(dS)_{V,E} > 0, (dG)_{T,P} < 0$.

21. (b) Only high pressure favours the conversion.

22. (d) By 2× (ii) – (i) – (iii)

$$H_{2(g)} + 2C_{(s)} \to C_2H_{2(g)},\ \Delta G^\circ = 209kJ\ .$$

23. (b) $\Delta G = -2.303RT \log K'$, Here $R = 2cal,\ T = 300K$

$$K' = \frac{10 \times 15}{3 \times 5} = 10\,;$$

$$\Delta G = -2.303 \times 2 \times 300 \times \log_{10} 10$$

$$= -2.303 \times 2 \times 300 \times 1 = -1381.8\,cal$$

24. (a) $\Delta G = \Delta H - T\Delta S$ (Gibb's free energy equation)

25. (d) $\Delta G = \Delta H - T\Delta S$

$\Delta G = -382.64 - (-145.6)\times 10^{-3} \times 298$

$= -339.3\,KJ\ mol^{-1}$

26. (d) $\Delta G = \Delta H - T\Delta S$; $\Delta G = \Delta E + P\Delta V - T\Delta S$

For spontaneity $(\Delta G = -ve)$

$\because\ \Delta G = -ve$, $\Delta E = +ve$

27. (a) $\Delta G = \Delta H - T\Delta S = 31400 - 1273\times 32$

$= 31400 - 40736 = -9336\,cal$

28. (d) $\Delta G = \Delta H - T\Delta S$

$0 = +30.558 - T\times 0.066$

or $T = \frac{30.558}{0.066} = 463K$

If $(dG)_{T,P} = 0$ sign '=' mean. If is reversible process

Critical Thinking Questions

1. (b) Due to randomness of particles is reduced since entropy decreases.

2. (c) $\Delta H = nCp\,\Delta T$

The process is isothermal therefore

$\Delta G = 0$; $\therefore\ \Delta H = 0$

3. (d) $13.7\ kcal = 57\,kJ = 5.7\times 10^{4}\,J$.

4. (b) When strong acid and strong base neutralize each other than the value of heat generated is about 13.7 *kcal*.

5. (b) Due to fall in temperature.

6. (d) $q_p = \Delta H$.

7. (d) $W = 2.303\,RT\,\log\frac{V_2}{V_1}$. As it involves the ratio $\frac{V_2}{V_1}$, volume can be used in any units. (R should be in joules).

8. (b) $-\frac{dQ}{dW} = \frac{dQ}{dQ - dE}$; $dE = dW + dQ$;

$-dW = dQ - dE$

$= \frac{nc_p\,dT}{nc_p dT - nc_v dT} = \frac{c_p}{(c_p - c_v)}$

$= \frac{7R}{2R}$ {for diatomic of gas $c_p = \frac{7R}{2}$}

9. (a) $C_2H_2(g) + H_2(g) \rightarrow C_2H_4(g)$

$\Delta ng = 1 - 2 = -1$; $\Delta H = -0.31\,KJ\ mol^{-1}$

$P = 1.5\,atm$, $\Delta V = -50\,mL = -0.050\,L$

$\Delta H = \Delta E + P\Delta V$

$-0.31 = \Delta E - 0.0076$; $\Delta E = -0.3024\,KJ$

10. (a) Since process is exothermic then heat is evolved due to this temperature of water increases.

11. (a) Because randomness is decreases.

12. (c) Conversion of graphite into diamond is an endothermic reaction. So, heat of diamond is higher than that of graphite. But ΔS would be negative for the conversion of graphite into diamond.

13. (c) ΔH and ΔS both are $+ve$ for spontaneous change, and $\Delta H = +ve$ for endothermic reaction.

14. (a) $\Delta G = \Delta H - T\Delta S$ is negative for spontaneity.

15. (a) Entropy (a measure of disorder) of universe is increasing toward maximum. This is II law of thermodynamics.

16. (a) For a pure substance T_A and T_B represent the same temperature. Hence A is a correct choice.

17. (a) For endothermic reaction enthalpy of products (H_P) > enthalpy of reactant (H_R)

Hence, change in enthalpy,

$\Delta H = H_P - H_R =$ Positive

18. (d) Suppose the no. of *gm*, 1*gm* for each case so the max. no of mole expected for $SO_2(g)$ which has to expected maximum entropy.

19. (b) $2Al + \frac{3}{2}O_2 \rightarrow Al_2O_3$, $\Delta H = -1596\,kJ$ .....(i)

$2Cr + \frac{3}{2}O_2 \rightarrow Cr_2O_3$, $\Delta H = -1134\,kJ$ .....(ii)

By (i) – (ii)

$2Al + Cr_2O_3 \rightarrow 2Cr + Al_2O_3$, $\Delta H = -462\,kJ$

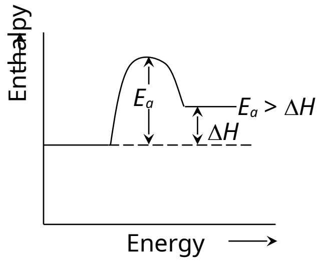
.

20. (a) Bomb calorimeter is used to measure heat of reaction.

21. (b) Larger the number of *C* and *H* atoms, greater is the heat of combustion.

22. (c) The bomb calorimeter is used to measure ΔE .

23. (c)



24. (b) $\Delta H_{\text{Neutralization}} = -57.1\,kJ = -13.7\,kcal$.

25. (b) Backmann thermometer is used to measure low temperature.

26. (b) Heat required to rise the temperature of a body by 1*K* called thermal capacity of the body.

27. (e) Mechanical work is important only in gases as they undergo appreciable change in volume.

28. (d) It is Lavoisier and Laplace law. This is another law of thermochemistry which was put forward before Hess's law.

29. (a) It is also known as "constant heat summation" law. It state that the total amount of heat evolved or absorbed in a reaction is same whether the reaction takes place in one step or in a number of steps.

30. (c) In this reaction $\Delta n = 2 - 4 = -2$ so $\Delta H \neq \Delta E$.

31. (a) $Q = \dfrac{18.94 \times 0.632 \times 0.998 \times 122}{1.89} =$

$771.1\ Kcal$

32. (c) $\Delta H = E_a$ for forward reaction $-E_a$ for backward reaction $= 19 - 9 = 10\,kJ$.

33. (d) $Q = 18.94 \times 0.632 \times 0.998 \times 1000$

$-57.4 + x = -12.13$

$x = 45.2$

34. (c) Thermodynamics is a reversible process in which surroundings are always equilibrium with system.

35. (a)

$$1\,cal = 4.18J = 4.18 \times 10^7\,erg = \frac{4.18}{1.602} \times 10^{19}\,eV$$

.

36. (b) Order of bond energy : $Cl_2 > Br_2 > F_2 > I_2$.

37. (c) Heat energy is also involved when one allotropic form of an element is converted in to another. graphite is the stabler allotrope because the heat of transformation of $C_{(diamond)} \to C_{(graphite)}$.

(i) $C_{(dia)} + O_{2(g)} = CO_{2(g)} \Delta H = -94.5\,kcal$

(ii)

$C_{(graphite)} + O_{2(g)} = CO_{2(g)} \Delta H = -94.0\,k\,cal$

$\Delta H_{transformation} = -94.5 - (-94.0)$

$= -0.5\,k\,cal$.

38. (b) The compound *Y* possess less energy than the *X* and thus *Y* is more stable than *X*.

39. (c) Both ΔH and Δp are positive.

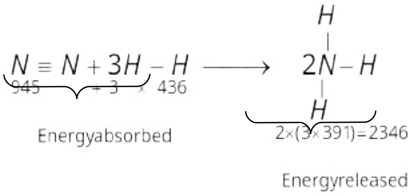
40. (a) For equilibrium $\Delta G^0 = 0$.

41. (b) Equilibrium constant is decreases with temperature and ΔH is also decreases so it is –*ve*.

42. (a) The fusion temperature of napthalene is minimum, because it is non-polar covalent compound and has less fusion temperature.

43. (a) The bond energy of $C - H$ bond is *y kcal* mol^{-1}.

44. (a)



$$\underbrace{N \equiv N + 3H}_{945 + 3 \times 436} - H \longrightarrow \underbrace{2N(-H)_3}_{2\times(3\times391)=2346}$$

Net. energy released = 2346 – 2253 = 93 k*J*

i.e. Δ*H* = – 93 *kJ* .

45. (d) If $E = +ve$ than the cell reaction will be spontaneous.

46. (d) All are the correct statements.

47. (d) $CH_2 = CH_{2(g)} + H_{2(g)} \rightarrow H_3C - CH_{3(g)}$

$414 \times 4 = 1656$ $\qquad$ $414 \times 6 = 2484$

$615 \times 1 = 615$ $\qquad$ $347 \times 1 = 347$

$435 \times 1 = \underline{435}$ $\qquad$ 2831

2706

$\Delta H = 2706 - 2831 = -125\,kJ$

48. (b) It means that the heat absorbed when one gram molecule of HCl is formed from its elements at $298K$ is

$= 22.060\,k\,cal$.

49. (d) *eq*. (i) + *eq*. (ii) find the required result and divide by 2.

50. (d) For complete neutralization of strong acid and strong base energy released is $57.32\,KJ\ /mol$

No. of mole of $H_2SO_4 = \dfrac{0.2 \times 50}{1000} = 10^{-2}$

No. of mole of $KOH = \dfrac{1}{1000} \times 50 = 5 \times 10^{-2}$

So $= 57.32 \times 10^{-2} = 0.5732 KJ$
$= 573.2$ *Joule* .

51. (b) For Combustion reaction, ΔH is negative, $\Delta n = (16+18) - (25+2) = +7$, so ΔS is $+ve$, reaction is spontaneous, hence ΔG is –*ve*.

52. (a) $\Delta G = \Delta H - T\Delta S$, $T = 27 + 273 = 300 K$

$$\Delta G = (-285.8) - (300)(-0.163) = -236.9 kJ\ m$$

Assertion & Reason

1. (b) Assertion and reason show, reaction at equilibrium state in which $\Delta G = 0$, $\Delta S = 0$, $\Delta H = 0$.

2. (b) It is correct that on touching the ice we feel cold because ice absorb heat from our hand.

3. (b) Entropy of ice is less than water because water molecules in solid state lose kinetic energy and hence their tendency of movement minimise. Hence entropy decrease in solid state. The reason that ice have cage like structure is also correct but reason is not or correct explanation for assertion.

4. (c) During isothermal expansion of an ideal gas against vacuum is zero because expansion is isothermal. The reason, that volume occupied by the molecules of an ideal gas is zero, is false.

5. (a) it is fact that absolute values of internal energy of substances can not be determined. It is also true that to determine exact values of constituent energies of the substance is impossible.

6. (b) Mass and volume are extensive properties. mass/volume is also an extensive parameter. Here, both assertion and reason are true.

7. (b) The molar entropy of vaporization of water it differ from ethanol due to hydrogen bonding according to VSEPR theory water molecule having two lone pair of electron by which it angular and show some polarity which is higher than that of ethanol so both assertion and reason are correct but reason is not explaination assertion.

8. (a) The assertion that the increase in internal energy for the vaporisation of one mole of water at 1 *atm* and 373 *K* is zero is true and this is because that for all isothermal process internal energy is zero.

9. (b) $N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$

We know that $\Delta H = \Delta E + \Delta nRT$

$\Delta n = 2 - 2 = 0$ hence, $\Delta nRT = 0$

Therefore, $\Delta H = \Delta E$

10. (a) The enthalpies of neutralisation of strong acids and strong bases are same they are 13.7 Kcal. The reason is that it is heat of formation of water from H^+ and OH^- ions. $H^+ + OH^- \rightarrow H_2O, \Delta H = 13.7 Kcal$. Thus, both assertion and reason are true.

11. (a) Zeroth (law of temperature) can also be summarized as two objects at different temperature in thermal contact with each other tend to move towards the same temperature.

12. (d) Photo chemical reactions have $+ve\ \Delta G$.

14. (e) Heat absorbed in a reaction at constant temperature and constant volume $(Qv) = E$.

15. (c) Values of state functions depend only on the state of the system and not on how it is reached.

16. (a) The properties whose magnitude depends upon the quantity of matter present in the system are called extensive properties.

17. (c) Combustion reactions are always accompanied by the evolution of heat therefore, for such reactions the value of ΔH is always negative.

18. (b) In an isothermal process change in internal energy (ΔE) is zero (as it is a fucntion of temperature). $\therefore$ According to first law of thermodynamics

$\because q + w = \Delta E$, hence $Q = -W$ (if $\Delta E = 0$)

If a system undergoes a change in which internal energy of the system remains constant (*i.e.,* $\Delta E = 0$), then $-W = Q$.

This means that work done by the system equals the heat absorbed by the system.

20. (e) If a refrigerator's door is kept open room gets heated as heat energy is released to the surroundings.

21. (c) Enthalpy is zero but entropy is not zero. Vibrational motion exists even at absolute zero.

22. (c) It may involve increase or decrease in temperature of the system. Systems in which such process occur, are thermally insulated from the surroundings.

Thermodynamics and Thermochemistry

SET Self Evaluation Test -10

1. The internal energy change when a system goes from state *A* to *B* is 40 *kJ/mole*. If the system goes from *A* to *B* by a reversible path and returns to state *A* by an irreversible path what would be the net change in internal energy

[CBSE PMT 2003]

(a) 40 *kJ* (b) > 0 *kJ*

(c) < 40 *kJ* (d) Zero

2. The correct relationship is **[DPMT 2002]**

(a) $\Delta H + P\Delta V = \Delta V$ (b) $\Delta H - \Delta nRT = \Delta E$

(c) $\Delta E + \Delta nRT = \Delta P$ (d) None of these

3. For $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$ at 977^oC; $\Delta H = 176$ *kJ mol*, then ΔE is **[BVP 2003]**

(a) 180 *kJ* (b) 186.4 *kJ*

(c) 165.6 *kJ* (d) 160 *kJ*

4. Values of ΔH and ΔS for five different reactions are given below.

Reaction	$\Delta H\,(kJ\ mol^{-1}$	$\Delta S\,(JK^{-1}\ mo$
I	+98.0	+14.8
II	– 55.5	–84.6
III	+28.3	–17.0
IV	– 40.5	+24.6
V	+ 34.7	0.0

On the basis of these values predict which one of these will be spontaneous at all tempeature

[Kerala PMT 2004; KCET 1988,90]

(a) Reaction I (b) Reaction II

(c) Reaction III (d) Reaction IV

(e) Reaction V

5. Molar heat capacity of water in equilibrium with ice at constant pressure is **[IIT JEE 1997]**

(a) Zero (b) Infinity (∞)

(c) $40.45 kJ\ K^{-1} mol^{-1}$ (d) $75.48 J\ K^{-1}$

6. Internal energy does not include

[AIIMS 1999; CPMT 2000]

(a) Nuclear energy

(b) Rotational energy

(c) Vibrational energy

(d) Energy arising by gravitational pull

7. Two moles of an ideal gas expand spontaneously into a vacuum. The work done is **[AMU 2000]**

(a) 2 *Joule* (b) 4 *Joule*

(c) Zero (d) Infinite

8. Heat exchanged in a chemical reaction at constant temperature and constant pressure is called as

[BHU 1998; Pb. PET 2000; MP PET 2002]

(a) Internal energy (b) Enthalpy

(c) Entropy (d) Free energy

9. Which of the following statements is true **[KCET 2002]**

(a) ΔE is always greater than ΔH

(b) ΔE is always less than ΔH

(c) ΔE may be lesser or greater or equal to ΔH

(d) ΔE is always proportional to ΔH

10. Mass and energy are conserved is demonstrated by

[MH CET 2002]

(a) First law of thermodynamics

(b) Law of conservation of energy

(c) Law of conservation of mass

(d) Modified form of Ist law of thermodynamics

11. The enthalpy of the reaction,

$H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(g)$ is ΔH_1 and that of

$H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(l)$ is ΔH_2. Then **[KCET 2004]**

(a) $\Delta H_1 < \Delta H_2$ (b) $\Delta H_1 + \Delta H_2 = 0$

(c) $\Delta H_1 > \Delta H_2$ (d) $\Delta H_1 = \Delta H_2$

12. A reaction occurs spontaneously if

[MP PET 2002; CBSE PMT 2005]

(a) $T\Delta S < \Delta H$ and both ΔH and ΔS are +ve

(b) $T\Delta S > \Delta H$ and both ΔH and ΔS are +ve

(c) $T\Delta S = \Delta H$ and both ΔH and ΔS are +ve

(d) $T\Delta S > \Delta H$ and ΔH is +ve and ΔS is –ve

13. Which expression is correct for the work done in adiabatic reversible expansion of an ideal gas **[AMU 2002]**

(a) $W = nRT \ln\frac{V_2}{V_1}$ (b) $W = n_e \ln\frac{T_2}{T_1}$

(c) $W = P\Delta V$ (d) $W = -\int_1^2 PdV$

14. If an endothermic reaction is non-spontaneous at freezing point of water and becomes feasible at its boiling point, then

[AIEEE 2002]

(a) ΔH is $-ve$, ΔS is +*ve*

(b) ΔH and ΔS both are +*ve*

(c) ΔH and ΔS both are –*ve*

(d) ΔH is +*ve*, ΔS is –*ve*

15. What is the entropy change (in $JK^{-1}\, mol^{-1}$) when one mole of ice is converted into water at 0^oC (The enthalpy change for the conversion of ice to liquid water is 6.0 *kJ* mol^{-1} at 0^oC) **[CBSE PMT 2003]**

(a) 21.98 (b) 20.13

(c) 2.013 (d) 2.198

16. One mole of $NaCl$ (*s*) on melting absorbed $30.5\,kJ$ of heat and its entropy is increased by $28.8\,JK^{-1}$. The melting point of $NaCl$ is **[DPMT 2004]**

(a) 1059 *K* (b) 30.5 *K*

(c) 28.8 *K* (d) 28800 *K*

17. The enthalpy change (ΔH) for the process $N_2H_4(g) \rightarrow 2N(g) + 4H(g)$ in $1724\,KJ\ mol^{-1}$. If the bond energy of $N-H$ bond in ammonia is $391\,KJ\ mol^{-1}$. What is the bond energy of $N-N$ bond is N_2H_4

[MP PMT 2004]

(a) $160\,KJ\ mol^{-1}$ (b) $391\,KJ\ mol^{-1}$

(c) $1173\,KJ\ mol^{-1}$ (d) $320\,KJ\ mol^{-1}$

18. Liquid ammonia is used in refrigeration because of its

[DCE 2003]

(a) High dipole moment

(b) High heat of vaporisation

(c) High basicity

(d) All of these

19. A cylinder of gas supplied by Bharat Petroleum is assumed to contain $14\,kg$ of butane. It a normal family requires $20{,}000\,kJ$ of energy per day for cooking, butane gas in the cylinder last for …. Days **[Kerala PMT 2004]**

(ΔH_c of $C_4H_{10} = -2658\,KJ\ per\, mole$)

(a) 15 days (b) 20 days

(c) 50 days (d) 40 days

(e) 32 days

20. The heat of neutralization of HCl by $NaOH$ under certain condition is – 55.9 *kJ* and that of HCN by $NaOH$ is –12.1 *kJ*. the heat of ionization of HCN is **[MP PET 2001]**

(a) $-68.0\,kJ\ mol^{-1}$ (b) $-43.8\,kJ\ mol^{-1}$

(c) $68.0\,kJ\ mol^{-1}$ (d) $43.8\,kJ\ mol^{-1}$

21. Equilibrium constant of a reaction is related to

[AIIMS 1991]

(a) Standard free energy change ΔG^o

(b) Free energy change ΔG

(c) Temperature *T*

(d) None

22. The standard Gibbs free energy change ΔG^o is related to equilibrium constant K_p as **[MP PET/PMT 1998]**

(a) $K_p = -RT \ln \Delta G^o$ (b) $K_p = \left(\frac{e}{RT}\right)^{\Delta G^o}$

(c) $K_p = -\frac{\Delta G^o}{RT}$ (d) $K_p = e^{-\frac{\Delta G^o}{RT}}$

23. The standard enthalpy or the decomposition of N_2O_5 to NO_2 is 58.04 kJ and standard entropy of this reaction is $176.7 J/K$. The standard free energy change for this reaction at $25^o C$ is **[DCE 2004]**

(a) –5.38 *kJ* (b) 5.38 *kJ*

(c) 5.38 *kJ* (d) –538 *kJ*

24. For the equilibrium $H_2O(l) \rightleftharpoons H_2O(g)$ at 1 atm and 298 *K*

[AIIMS 2004]

(a) Standard free energy change is equal to zero $(G\Delta^o = 0)$

(b) Free energy change is less than zero $(\Delta G < 0)$

(c) Standard free energy change is less than zero $(\Delta G^o < 0)$

(d) Standard free energy change is greater than zero $(\Delta G^o > 0)$

25. For reaction $Ag_2O(s) \rightarrow 2Ag(s) + (1/2)O_2(g)$ the value of $\Delta H = 30.56\ kJ\ mol^{-1}$ and $\Delta S = 0.066\ kJK^{-1}\ mol^{-1}$. Temperature at which free energy change for reaction will be zero, is **[MH CET 1999]**

(a) 373 *K* (b) 413 *K*

(c) 463 *K* (d) 493 *K*

AS Answers and Solutions

(SET -10)

1. (d) $A \longrightarrow B$

$A \xleftarrow{-40} B$

$\Delta H = 40 - 40 = 0$.

2. (b) $\Delta H = \Delta E + \Delta nRT$.

3. (c) $\Delta n = 1 - 0 = 1$

$\Delta E = \Delta H + \Delta nRT$

$$\Delta E = +176 - 1 \times \frac{8.314}{1000} \times 1240 = 165.6 kJ.$$

4. (d) A spontaneous process is accompanied by decrease in enthalpy and increase in entropy means ΔH is negative and ΔS is positive.

5. (b) $C_P = \left(\frac{\delta H}{\delta T}\right)_P$, At equilibrium *T* is constant *i.e.* $\delta T = 0$, thus $C_P = \infty$.

6. (d) $E = E_{ele.} + E_{nucl.} + E_{chemical} + E_{potentia}$

$+ E_{kinetic}(E_t + E_v + E_r)$.

7. (c) An ideal gas under going expansion in vacuum shows, $\Delta E = 0, W = 0$ and $q = 0$.

8. (b) $\Delta H = q_p$.

9. (c) ΔE may be greater or lesser or equal to ΔH.

$\because \Delta H = \Delta E + P\Delta V = \Delta E + \Delta nRT$.

10. (d) It is a modified form of Ist law of thermodynamics. It is a conservation law of mass and energy.

11. (a) for reaction (i) $\Delta n_1 = 0.5$

for reaction (ii) $\Delta n_2 = 1.5$

So, $\Delta H_1 < \Delta H_2$

12. (b) *For spontaneous reaction* ΔG *should be negative*

$\Delta G = \Delta H - T\Delta S = (+ve) - T(+ve)$

If $T\Delta S > \Delta H$ *then* ΔG *will be negative and reaction will be spontaneous.*

13. (b) $W = P\Delta V$.

14. (b) ΔH and ΔS both are *+ve* than reaction is spontaneous.

15. (a) $\Delta S = \frac{q_{rev}}{T} = \frac{6000}{273} = 21.98 JK^{-1}mol^{-1}$

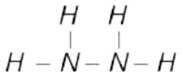
16. (a) $NaCl(s) \rightleftharpoons NaCl(l)$

Given that : $\Delta H = 30.5 KJ\ mol^{-1}$

$\Delta S = 28.8 JK^{-1} = 28.8 \times 10^{-3}\ KJ\ K^{-1}$

By using $\Delta S = \frac{\Delta H}{T}$

$$= \frac{30.5}{28.8 \times 10^{-3}} = 1059 K$$

17. (a) 

$H-\overset{H}{\underset{|}{N}}-\overset{H}{\underset{|}{N}}-H$ (So, $4N-H$ bond present)

means their energy $= 391 \times 4 = 1564$

so the bond energy of $N-N$ in N_2H_4

$= 1724 - 1564 = 160 KJ\ /mol$

18. (b) Ammonia has high heat of vaporisation hence is used in refrigeration.

19. (e) Calorific value of butane

$$= \frac{\Delta H_c}{\text{mol.wt.}} = \frac{2658}{58} = 45.8\,KJ\ /gm$$

Cylinder consist $14Kg$ of butane means $14000gm$ of butane

$\because 1gm$ gives $45.8\,KJ$

$\therefore 14000gm$ gives 14000×45.8

$= 641200KJ$

Family need $20{,}000\,KJ\ /day$

So gas full fill the requirement for

$$\frac{641200}{20{,}000} = 32.06\,days$$

20. (d)

21. (a) $\Delta G^o = -2.303 \log k.$

22. (d) $K_p = e^{-\Delta G^o / RT}$.

23. (d)

24. (b) For reaction $H_2O(l) \rightleftharpoons H_2O(g)$

$\Delta n = 1$ means positive

so when Δn is positive then $\Delta G < 0$.

25. (c) $\Delta G = \Delta H - T\Delta S$

$\Delta G = 0$ at equilibrium

$\therefore \Delta H = T\Delta S$ or $30.56 = T \times 0.066$

$T = 463K$.

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Chemical Arithmetics

OT Ordinary Thinking

Objective Questions

Significant figures, Units for measurement, Matter and Separation of mixture

1. One fermi is **[Haryana CEET 1994; DPMT 2004]**

(a) $10^{-13}\,cm$ (b) $10^{-15}\,cm$

(c) $10^{-10}\,cm$ (d) $10^{-12}\,cm$

2. A picometre is written as

(a) $10^{-9}\,m$ (b) $10^{-10}\,m$

(c) $10^{-11}\,m$ (d) $10^{-12}\,m$

3. One atmosphere is equal to

(a) 101.325 K pa (b) 1013.25 $K\,pa$

(c) $10^5\,Nm$ (d) None of these

4. Dimensions of pressure are same as that of **[CBSE PMT 1995]**

(a) Energy (b) Force

(c) Energy per unit volume (d) Force per unit volume

5. The prefix 10^{18} is **[Kerala MEE 2002]**

(a) Giga (b) Nano

(c) Mega (d) Exa

6. Given the numbers : 161cm, 0.161cm, 0.0161 cm. The number of significant figures for the three numbers are **[CBSE PMT 1998]**

(a) 3, 4 and 5 respectively (b) 3, 3 and 3 respectively

(c) 3, 3 and 4 respectively (d) 3, 4 and 4 respectively

7. Significant figures in 0.00051 are

(a) 5 (b) 3

(c) 2 (d) 4

8. Which of the following halogen can be purified by sublimation **[Manipal PMT 2001]**

(a) F_2 (b) Cl_2

(c) Br_2 (d) I_2

9. Difference in density is the basis of **[Kerala MEE 2002]**

(a) Ultrafiltration (b) Molecular sieving

(c) Gravity Separation (d) Molecular attraction

10. Which of the following elements of matter would best convey that there is life on earth

(a) Oxygen (b) Hydrogen

(c) Carbon (d) Iron

11. The compound which is added to table salt for maintaining proper health is

(a) KCl (b) KBr

(c) NaI (d) $MgBr_2$

12. Which of the following contains only one element

(a) Marble (b) Diamond

(c) Glass (d) Sand

13. In known elements, the maximum number is of **[CPMT 1985]**

(a) Metals (b) Non-metals

(c) Metalloids (d) None of these

14. Which one of the following is not an element

(a) Diamond (b) Graphite

(c) Silica (d) Ozone

15. A mixture of $ZnCl_2$ and $PbCl_2$ can be separated by **[AFMC 1989]**

(a) Distillation (b) Crystallization

(c) Sublimation (d) Adding aceitic acid

16. A mixture of methyl alcohol and acetone can be separated by **[Manipal PMT 2001]**

(a) Distillation

(b) Fractional distillation

(c) Steam distillation

(d) Distillation under reduced pressure

17. In the final answer of the expression $\dfrac{(29.2-20.2)(1.79\times10^5)}{1.37}$. The number of significant figures is **[CBSE PMT 1994]**

(a) 1 (b) 2

(c) 3 (d) 4

18. 81.4 g sample of ethyl alcohol contains 0.002 g of water. The amount of pure ethyl alcohol to the proper number of significant figures is

(a) 81.398 g (b) 71.40 g

(c) 91.4 g (d) 81 g

19. The unit $J\,Pa^{-1}$ is equivalent to

(a) m^3 (b) cm^3

(c) dm^3 (d) None of these

20. From the following masses, the one which is expressed nearest to the milligram is

(a) 16 *g* (b) 16.4 *g*

(c) 16.428 *g* (d) 16.4284 *g*

21. The number of significant figures in 6.02×10^{23} is

(a) 23 (b) 3

(c) 4 (d) 26

22. The prefix zepto stands for **[DPMT 2004]**

(a) 10^{9} (b) 10^{-12}

(c) 10^{-15} (d) 10^{-21}

23. The significant figures in 3400 are **[BHU 2004]**

(a) 2 (b) 5

(c) 6 (d) 4

24. The number of significant figures in 6.0023 are **[Pb.CET 2001]**

(a) 5 (b) 4

(c) 3 (d) 1

25. Given $P = 0.0030m$, $Q = 2.40m$, $R = 3000m$, Significant figures in P, Q and R are respectively **[Pb. CET 2002]**

(a) 2, 2, 1 (b) 2, 3, 4

(c) 4, 2, 1 (d) 4, 2, 3

26. The number of significant figures in 60.0001 is **[Pb. CET 2000]**

(a) 5 (b) 6

(c) 3 (d) 2

27. A sample was weighted using two different balances. The result's were (i) 3.929 *g* (ii) 4.0 *g*. How would the weight of the sample be reported

(a) 3.929 *g* (b) 3 *g*

(c) 3.9 *g* (d) 3.93 *g*

Laws of chemical combination

1. Which of the following pairs of substances illustrate the law of multiple proportions **[CPMT 1972, 78]**

(a) CO and CO_2 (b) H_2O and D_2O

(c) $NaCl$ and $NaBr$ (d) MgO and $Mg(OH)_2$

2. 1.0 *g* of an oxide of *A* contained 0.5 *g* of *A*. 4.0 *g* of another oxide of *A* contained 1.6 *g* of *A*. The data indicate the law of

(a) Reciprocal proportions (b) Constant proportions

(c) Conservation of energy (d) Multiple proportions

3. Among the following pairs of compounds, the one that illustrates the law of multiple proportions is

(a) NH_3 and NCl_3 (b) H_2S and SO_2

(c) CuO and Cu_2O (d) CS_2 and $FeSO_4$

4. The percentage of copper and oxygen in samples of CuO obtained by different methods were found to be the same. This illustrates the law of **[AMU 1982, 92]**

(a) Constant proportions (b) Conservation of mass

(c) Multiple proportions (d) Reciprocal proportions

5. Two samples of lead oxide were separately reduced to metallic lead by heating in a current of hydrogen. The weight of lead from one oxide was half the weight of lead obtained from the other oxide. The data illustrates **[AMU 1983]**

(a) Law of reciprocal proportions

(b) Law of constant proportions

(c) Law of multiple proportions

(d) Law of equivalent proportions

6. Chemical equation is balanced according to the law of **[AMU 1984]**

(a) Multiple proportion (b) Reciprocal proportion

(c) Conservation of mass (d) Definite proportions

7. Avogadro number is

(a) Number of atoms in one gram of element

(b) Number of millilitres which one mole of a gaseous substances occupies at NTP

(c) Number of molecules present in one gram molecular mass of a substance

(d) All of these

8. Different propartions of oxygen in the various oxides of nitrogen prove the **[MP PMT 1985]**

(a) Equivalent proportion (b) Multiple proportion

(c) Constant proportion (d) Conservation of matter

9. Two elements *X* and *Y* have atomic weights of 14 and 16. They form a series of compounds *A*, *B*, *C*, *D* and *E* in which the same amount of element *X*, *Y* is present in the ratio 1 : 2 : 3 : 4 : 5. If the compound *A* has 28 parts by weight of *X* and 16 parts by weight of *Y*, then the compound of *C* will have 28 parts weight of *X* and **[NCERT 1971]**

(a) 32 parts by weight of *Y* (b) 48 parts by weight of *Y*

(c) 64 parts by weight of *Y* (d) 80 parts by weight of *Y*

10. Carbon and oxygen combine to form two oxides, carbon monoxide and carbon dioxide in which the ratio of the weights of carbon and oxygen is respectively 12 : 16 and 12 : 32. These figures illustrate the

(a) Law of multiple proportions

(b) Law of reciprocal proportions

(c) Law of conservation of mass

(d) Law of constant proportions

11. A sample of calcium carbonate $(CaCO_3)$ has the following percentage composition : *Ca* = 40%; *C* = 12%; *O* = 48%

If the law of constant proportions is true, then the weight of calcium in 4 *g* of a sample of calcium carbonate obtained from another source will be

(a) 0.016 *g* (b) 0.16 *g*

(c) 1.6 *g* (d) 16 *g*

12. *n g* of substance *X* reacts with *m g* of substance *Y* to form *p g* of substance *R* and *q g* of substance *S*. This reaction can be represented as, $X + Y = R + S$. The relation which can be established in the amounts of the reactants and the products will be

(a) $n - m = p - q$ (b) $n + m = p + q$

(c) $n = m$ (d) $p = q$

13. Which of the following is the best example of law of conservation of mass **[NCERT 1975]**

(a) 12 *g* of carbon combines with 32 *g* of oxygen to form 44 *g* of CO_2

(b) When 12 *g* of carbon is heated in a vacuum there is no change in mass

(c) A sample of air increases in volume when heated at constant pressure but its mass remains unaltered

(d) The weight of a piece of platinum is the same before and after heating in air

14. The law of multiple proportions is illustrated by the two compounds **[NCERT 1972]**

(a) Sodium chloride and sodium bromide

(b) Ordinary water and heavy water

(c) Caustic soda and caustic potash

(d) Sulphur dioxide and sulphur trioxide

15. In compound *A*, 1.00 *g* nitrogen unites with 0.57 *g* oxygen. In compound *B*, 2.00 *g* nitrogen combines with 2.24 *g* oxygen. In compound *C*, 3.00 *g* nitrogen combines with 5.11 *g* oxygen. These results obey the following law **[CPMT 1971]**

(a) Law of constant proportion

(b) Law of multiple proportion

(c) Law of reciprocal proportion

(d) Dalton's law of partial pressure

16. Hydrogen combines with oxygen to form H_2O in which 16 *g* of oxygen combine with 2 *g* of hydrogen. Hydrogen also combines with carbon to form CH_4 in which 2 *g* of hydrogen combine with 6 *g* of carbon. If carbon and oxygen combine together then they will do show in the ratio of

(a) 6 : 16 or 12 : 32 (b) 6 : 18

(c) 1 : 2 (d) 12 : 24

17. 2 *g* of hydrogen combine with 16 *g* of oxygen to form water and with 6 *g* of carbon to form methane. In carbon dioxide 12 *g* of carbon are combined with 32 *g* of oxygen. These figures illustrate the law of

(a) Multiple proportions (b) Constant proportions

(c) Reciprocal proportions (d) Conservation of mass

18. An element forms two oxides containing respectively 53.33 and 36.36 percent of oxygen. These figures illustrate the law of

(a) Conservation of mass (b) Constant proportions

(c) Reciprocal proportions (d) Multiple proportions

19. After a chemical reaction, the total mass of reactants and products **[MP PMT 1989]**

(a) Is always increased (b) Is always decreased

(c) Is not changed (d) Is always less or more

20. A sample of pure carbon dioxide, irrespective of its source contains 27.27% carbon and 72.73% oxygen. The data support

[AIIMS 1992]

(a) Law of constant composition

(b) Law of conservation of mass

(c) Law of reciprocal proportions

(d) Law of multiple proportions

21. The law of definite proportions is not applicable to nitrogen oxide because **[EAMCET 1981]**

(a) Nitrogen atomic weight is not constant

(b) Nitrogen molecular weight is variable

(c) Nitrogen equivalent weight is variable

(d) Oxygen atomic weight is variable

22. Which one of the following pairs of compounds illustrates the law of multiple proportion

[EAMCET 1989]

(a) H_2O, Na_2O (b) MgO, Na_2O

(c) Na_2O, BaO (d) $SnCl_2, SnCl_4$

Atomic, Molecular and Equivalent masses

1. Which property of an element is always a whole number

[MP PMT 1986]

(a) Atomic weight
(b) Equivalent weight
(c) Atomic number
(d) Atomic volume

2. Which one of the following properties of an element is not variable **[Bihar MADT 1981]**

(a) Valency
(b) Atomic weight
(c) Equivalent weight
(d) All of these

3. The modern atomic weight scale is based on

[MP PMT 2002]

(a) C^{12}
(b) O^{16}
(c) H^1
(d) C^{13}

4. 1 *amu* is equal to

(a) $\frac{1}{12}$ of $C-12$
(b) $\frac{1}{14}$ of O - 16
(c) $1g$ of H_2
(d) 1.66×10^{-23} kg

5. Sulphur forms the chlorides S_2Cl_2 and SCl_2. The equivalent mass of sulphur in SCl_2 is

[EAMCET 1985; Pb. CET 2001]

(a) 8 *g*/mole
(b) 16 *g*/mole
(c) 64.8 *g*/mole
(d) 32 *g*/mole

6. The sulphate of a metal M contains 9.87% of *M*. This sulphate is isomorphous with $ZnSO_4.7H_2O$. The atomic weight of *M* is **[IIT 1991]**

(a) 40.3
(b) 36.3
(c) 24.3
(d) 11.3

7. When 100 *ml* of 1 M $NaOH$ solution and 10 ml of 10 N H_2SO_4 solution are mixed together, the resulting solution will be **[DPMT 1982]**

(a) Alkaline
(b) Acidic
(c) Strongly acidic
(d) Neutral

8. In chemical scale, the relative mass of the isotopic mixture of oxygen atoms (O^{16}, O^{17}, O^{18}) is assumed to be equal to

[Bihar MADT 1981]

(a) 16.002
(b) 16.00
(c) 17.00
(d) 11.00

9. For preparing 0.1 *N* solution of a compound from its impure sample of which the percentage purity is known, the weight of the substance required will be

[MP PET 1996]

(a) More than the theoretical weight
(b) Less than the theoretical weight
(c) Same as the theoretical weight
(d) None of these

10. 1 mol of CH_4 contains

(a) 6.02×10^{23} atoms of *H*
(b) 4 *g* atom of Hydrogen
(c) 1.81×10^{23} molecules of CH_4
(d) 3.0 *g* of carbon

11. In the reaction $2Na_2S_2O_3 + I_2 \rightarrow Na_2S_4O_6 + 2NaI$, the equivalent weight of $Na_2S_2O_3$ (mol. wt. = *M*) is equal to

(a) M
(b) $M/2$
(c) $M/3$
(d) $M/4$

12. When potassium permanganate is titrated against ferrous ammonium sulphate, the equivalent weight of potassium permanganate is

[CPMT 1988]

(a) Molecular weight /10
(b) Molecular weight /5
(c) Molecular weight /2
(d) Molecular weight

13. Boron has two stable isotopes, ^{10}B (19%) and ^{11}B (81%). The atomic mass that should appear for boron in the periodic table is **[CBSE PMT 1990]**

(a) 10.8
(b) 10.2
(c) 11.2
(d) 10.0

14. What is the concentration of nitrate ions if equal volumes of 0.1 M $AgNO_3$ and 0.1 M $NaCl$ are mixed together

[CPMT 1983; NCERT 1985]

(a) 0.1 *M*
(b) 0.2 *M*
(c) 0.05 *M*
(d) 0.25 *M*

15. Total number of atoms represented by the compound $CuSO_4.5H_2O$ is **[BHU 2005]**

(a) 27
(b) 21
(c) 5
(d) 8

16. 74.5 *g* of a metallic chloride contain 35.5 g of chlorine. The equivalent weight of the metal is

[CPMT 1986]

(a) 19.5
(b) 35.5
(c) 39.0
(d) 78.0

17. 7.5 grams of a gas occupy 5.8 litres of volume at STP the gas is

(a) NO
(b) N_2O
(c) CO
(d) CO_2

18. The number of atoms in 4.25 *g* of NH_3 is approximately

[CBSE PMT 1999; MH CET 2003]

(a) 1×10^{23}
(b) 2×10^{23}
(c) 4×10^{23}
(d) 6×10^{23}

19. One litre of a gas at STP weight 1.16 *g* it can possible be

[AMU 1992]

(a) C_2H_2 (b) CO

(c) O_2 (d) CH_4

20. The vapour density of a gas is 11.2. The volume occupied by 11.2 *g* of the gas at ATP will be **[Bihar CET 1995]**

(a) 11.2 *L* (b) 22.4 *L*

(c) 1 *L* (d) 44.8 *L*

21. Equivalent weight of crystalline oxalic acid is

[MP PMT 1995]

(a) 30 (b) 63

(c) 53 (d) 45

22. The equivalent weight of an element is 4. Its chloride has a V.D 59.25. Then the valency of the element is

[BHU 1997]

(a) 4 (b) 3

(c) 2 (d) 1

23. 1.25 *g* of a solid dibasic acid is completely neutralised by 25 *ml* of 0.25 molar $Ba(OH)_2$ solution. Molecular mass of the acid is

(a) 100 (b) 150

(c) 120 (d) 200

24. The oxide of a metal has 32% oxygen. Its equivalent weight would be **[MP PMT 1985]**

(a) 34 (b) 32

(c) 17 (d) 8

25. The mass of a molecule of water is

[Bihar CEE 1995]

(a) $3\times10^{-26}\,kg$ (b) $3\times10^{-25}\,kg$

(c) $1.5\times10^{-26}\,kg$ (d) $2.5\times10^{-26}\,kg$

26. 1.24 *gm P* is present in 2.2 *gm*

(a) P_4S_3 (b) P_2S_2

(c) PS_2 (d) P_2S_4

27. The atomic weights of two elements *A* and *B* are 40 and 80 respectively. If *x g* of *A* contains *y* atoms, how many atoms are present in 2*x g* of *B*

(a) $\frac{y}{2}$ (b) $\frac{y}{4}$

(c) *y* (d) 2*y*

28. Assuming fully decomposed, the volume of CO_2 released at STP on heating 9.85*g* of $BaCO_3$ (Atomic mass of *Ba*=137) will be **[CBSE PMT 2000]**

(a) 0.84 *L* (b) 2.24 *L*

(c) 4.06 *L* (d) 1.12 *L*

29. If N_A is Avogadro's number then number of valence electrons in 4.2 *g* of nitride ions (N^{3-})

(a) 2.4 N_A (b) 4.2 N_A

(c) 1.6 N_A (d) 3.2 N_A

30. The weight of 1×10^{22} molecules of $CuSO_4.5H_2O$ is

[IIT 1991]

(a) 41.59 *g* (b) 415.9 *g*

(c) 4.159 *g* (d) None of these

31. Rearrange the following (I to IV) in the order of increasing masses and choose the correct answer from (a), (b), (c) and (d) (Atomic mass: *N*=14, *O*=16, *Cu*=63).

I. 1 molecule of oxygen

II. 1 atom of nitrogen

III. 1×10^{-10} g molecular weight of oxygen

IV. 1×10^{-10} g atomic weight of copper

(a) II<I<III<IV (b) IV<III<II<I

(c) II<III<I<IV (d) III<IV<I<II

32. 1.520 *g* of the hydroxide of a metal on ignition gave 0.995 *gm* of oxide. The equivalent weight of metal is

[DPMT 1984]

(a) 1.520 (b) 0.995

(c) 19.00 (d) 9.00

33. How much coulomb charge is present on 1*g* ion of N^{3-}

(a) 5.2×10^6 Couloumb (b) 2.894×10^5 Couloumb

(c) 6.6×10^6 Couloumb (d) 8.2×10^6 Couloumb

34. Ratio of C_p and C_v of a gas X is 1.4, the number of atom of the gas 'X' present in 11.2 litres of it at NTP will be

[CBSE 1999]

(a) 6.02×10^{23} (b) 1.2×10^{23}

(c) 3.01×10^{23} (d) 2.01×10^{23}

35. If we consider that 1/6, in place of 1/12, mass of carbon atom is taken to be the relative atomic mass unit, the mass of one mole of a substance will **[AIEEE 2005]**

(a) Decrease twice

(b) Increase two fold

(c) Remain unchanged

(d) Be a function of the molecular mass of the substance

36. What should be the equivalent weight of phosphorous acid, if *P*=31; *O*=16; *H*=1

(a) 82 (b) 41

(c) 20.5 (d) None of these

37. The number of molecule at NTP in 1 *ml* of an ideal gas will be

(a) 6×10^{23} (b) 2.69×10^{19}

(c) 2.69×10^{23} (d) None of these

38. The specific heat of a metal is 0.16 its approximate atomic weight would be

(a) 32 (b) 16

(c) 40 (d) 64

39. The weight of a molecule of the compound $C_{60}H_{122}$ is

[AIIMS 2000]

(a) 1.4×10^{-21} g (b) 1.09×10^{-21} g

(c) 5.025×10^{23} g (d) 16.023×10^{23} g

40. What is the weight of oxygen required for the complete combustion of 2.8 *kg* of ethylene

[CBSE PMT 1989]

(a) 2.8 *kg* (b) 6.4 *kg*

(c) 9.6 *kg* (d) 96 *kg*

41. What volume of NH_3 gas at STP would be needed to prepare 100*ml* of 2.5 molal (2.5m) ammonium hydroxide solution

(a) 0.056 litres (b) 0.56 litres

(c) 5.6 litres (d) 11.2 litres

42. If the density of water is 1 $g\ cm^{-3}$ then the volume occupied by one molecule of water is approximately

[Pb. PMT 2004]

(a) $18\ cm^3$ (b) $22400\ cm^3$

(c) $6.02 \times 10^{-23}\ cm^3$ (d) $3.0 \times 10^{-23}\ cm^3$

43. Caffeine has a molecular weight of 194. If it contains 28.9% by mass of nitrogen, number of atoms of nitrogen in one molecule of caffeine is

(a) 4 (b) 6

(c) 2 (d) 3

44. A 400 *mg* iron capsule contains 100 mg of ferrous fumarate, $(CHCOO)_2Fe$. The percentage of iron pasent in it is approximately

(a) 33% (b) 25%

(c) 14% (d) 8%

45. The element whose a atom has mass of 10.86×10^{-26} *kg* is

(a) Boron (b) Calcium

(c) Silver (d) Zinc

46. The number of gram atoms of oxygen present in 0.3 gram mole of $(COOH)_2.2H_2O$ is

(a) 0.6 (b) 1.8

(c) 1.2 (d) 3.6

47. A gaseous mixture contains CH_4 and C_2H_6 in equimolecular proportion. The weight of 2.24 litres of this mixture at NTP is

(a) 4.6 *g* (b) 1.6 *g*

(c) 2.3 *g* (d) 23 *g*

48. Vapour density of a metal chloride is 66. Its oxide contains 53% metal. The atomic weight of the metal is

[Bihar MADT 1982]

(a) 21 (b) 54

(c) 27.06 (d) 2.086

49. One gram of hydrogen is found to combine with 80*g* of bromine one gram of calcium valency=2 combines with 4*g* of bromine the equivalent weight of calcium is

(a) 10 (b) 20

(c) 40 (d) 80

50. The equivalent weight of $MnSO_4$ is half its molecular weight when it is converted to

[IIT 1988; CPMT 1994]

(a) Mn_2O_3 (b) MnO_2

(c) MnO_4 (d) MnO_4^{2-}

51. $100\ mL$ of PH_3 on decomposition produced phosphorus and hydrogen. The change in volume is

[MNR 1986]

(a) $50\ mL$ increase (b) $500\ mL$ decrease

(c) $900\ mL$ decrease (d) Nil.

52. $12g$ of Mg (at. mass 24) on reacting completely with acid gives hydrogen gas, the volume of which at STP would be

[CPMT 1978]

(a) $22.4\ L$ (b) $11.2\ L$

(c) $44.8\ L$ (d) $6.1\ L$

53. Which of the following has least mass **[Pb. PET 1985]**

(a) $2\ g$ atom of nitrogen (b) 3×10^{23} atoms of C

(c) 1 mole of S (d) $7.0\ g$ of Ag

54. How many mole of helium gas occupy $22.4\ L$ at $0^{o}C$ at 1 atm. pressure **[Kurukshetra CEE 1992; CET 1992]**

(a) 0.11 (b) 0.90

(c) 1.0 (d) 1.11

55. Volume of a gas at STP is 1.12×10^{-7} cc. Calculate the number of molecules in it

[BHU 1997]

(a) 3.01×10^{20} (b) 3.01×10^{12}

(c) 3.01×10^{23} (d) 3.01×10^{24}

56. $4.4\ g$ of an unknown gas occupies $2.24 L$ of volume at standard temperature and pressure. The gas may be

[MP PMT 1995]

(a) Carbon dioxide (b) Carbon monoxide

(c) Oxygen (d) Sulphur dioxide

57. The number of moles of oxygen in $1\ L$ of air containing 21% oxygen by volume, in standard conditions, is

[CBSE PMT 1995; Pb. PMT 2004]

(a) 0.186 *mol* (b) 0.21 *mol*

(c) 2.10 *mol* (d) 0.0093 *mol*

58. The number of molecules in $8.96\ L$ of a gas at $0^{o}C$ and 1 atmosphere pressure is approximately **[BHU 1993]**

(a) 6.02×10^{23} (b) 12.04×10^{23}

(c) 18.06×10^{23} (d) 24.08×10^{22}

59. The equivalent weight of a metal is 9 and vapour density of its chloride is 59.25. The atomic weight of metal is

[Pb. CET 2002]

(a) 23.9 (b) 27.3

(c) 36.3 (d) 48.3

60. The molecular weight of a gas is 45. Its density at STP is

[Pb. PMT 2004]

(a) 22.4 (b) 11.2

(c) 5.7 (d) 2.0

61. Equivalent weight of a bivalent metal is 37.2. The molecular weight of its chloride is **[MH CET 2003]**

(a) 412.2 (b) 216

(c) 145.4 (d) 108.2

62. On reduction with hydrogen, 3.6 g of an oxide of metal left 3.2 g of metal. If the vapour density of metal is 32, the simplest formula of the oxide would be

[DPMT 2004]

(a) MO (b) M_2O_3

(c) M_2O (d) M_2O_5

63. The number of molecules in 4.25 *g* of ammonia are

[Pb. CET 2000]

(a) 0.5×10^{23} (b) 1.5×10^{23}

(c) 3.5×10^{23} (d) 1.8×10^{32}

The mole concept

1. Which one of the following pairs of gases contains the same number of molecules **[EAMCET 1987]**

(a) 16 *g* of O_2 and 14 *g* of N_2

(b) 8 *g* of O_2 and 22 *g* of CO_2

(c) 28 *g* of N_2 and 22 *g* of CO_2

(d) 32 *g* of O_2 and 32 *g* of N_2

2. Number of *gm* of oxygen in 32.2 *g* $Na_2SO_4.10H_2O$ is

[Haryana PMT 2000]

(a) 20.8 (b) 22.4

(c) 2.24 (d) 2.08

3. 250 *ml* of a sodium carbonate solution contains 2.65 grams of Na_2CO_3. If 10 *ml* of this solution is diluted to one litre, what is the concentration of the resultant solution (mol. wt. of Na_2CO_3 =106)

[EAMCET 2001]

(a) 0.1 *M* (b) 0.001 *M*

(c) 0.01 *M* (d) 10^{-4} *M*

4. A molar solution is one that contains one mole of a solute in

[IIT 1986]

(a) 1000 *g* of the solvent (b) One litre of the solvent

(c) One litre of the solution (d) 22.4 litres of the solution

5. The number of oxygen atoms in 4.4 *g* of CO_2 is approx.

[CBSE PMT 1990]

(a) 1.2×10^{23} (b) 6×10^{22}

(c) 6×10^{23} (d) 12×10^{23}

6. The volume occupied by 4.4 *g* of CO_2 at STP is

[AFMC 1997, 2004; Pb. CET 1997, 2002]

(a) 22.4 *L* (b) 2.24 *L*

(c) 0.224 *L* (d) 0.1 *L*

7. The number of water molecules present in a drop of water (volume 0.0018 *ml*) at room temperature is **[DCE 2000]**

(a) 6.023×10^{19} (b) 1.084×10^{18}

(c) 4.84×10^{17} (d) 6.023×10^{23}

8. One mole of calcium phosphide on reaction with excess of water gives **[IIT 1999]**

(a) One mole of phosphine

(b) Two moles of phosphoric acid

(c) Two moles of phosphine

(d) One mole of phosphorus pentoxide

9. 19.7 *kg* of gold was recovered from a smuggler. How many atoms of gold were recovered (*Au* =197) **[Pb. CET 1985]**

(a) 100 (b) 6.02×10^{23}

(c) 6.02×10^{24} (d) 6.02×10^{25}

10. The total number of protons in 10 *g* of calcium carbonate is ($N_0 = 6.023 \times 10^{23}$)

(a) 1.5057×10^{24} (b) 2.0478×10^{24}

(c) 3.0115×10^{24} (d) 4.0956×10^{24}

11. The number of molecules in 16 *g* of methane is

(a) 3.0×10^{23} (b) 6.02×10^{23}

(c) $\frac{16}{6.02} \times 10^{23}$ (d) $\frac{16}{3.0} \times 10^{23}$

12. Number of molecules in 100 *ml* of each of O_2, NH_3 and CO_2 at STP are

[Bihar MADT 1985]

(a) In the order $CO_2 < O_2 < NH_3$

(b) In the order $NH_3 < O_2 < CO_2$

(c) The same

(d) $NH_3 = CO_2 < O_2$

13. The molecular weight of hydrogen peroxide is 34. What is the unit of molecular weight

[MP PMT 1986]

(a) g (b) mol

(c) $g\,mol^{-1}$ (d) $mol\,g^{-1}$

14. The number of water molecules in 1 litre of water is

[EAMCET 1990]

(a) 18 (b) 18×1000

(c) N_A (d) $55.55\,N_A$

15. The number of electrons in a mole of hydrogen molecule is

[CPMT 1987]

(a) 6.02×10^{23} (b) 12.046×10^{23}

(c) 3.0115×10^{23} (d) Indefinite

16. The numbers of moles of $BaCO_3$ which contain 1.5 moles of oxygen atoms is **[EAMCET 1991]**

(a) 0.5 (b) 1

(c) 3 (d) 6.02×10^{23}

17. Which of the following is Loschmidt number

(a) 6×10^{23} (b) 2.69×10^{19}

(c) 3×10^{23} (d) None of these

18. How many molecules are present in one gram of hydrogen

[AIIMS 1982]

(a) 6.02×10^{23} (b) 3.01×10^{23}

(c) 2.5×10^{23} (d) 1.5×10^{23}

19. The total number of gm-molecules of SO_2Cl_2 in $13.5g$ of sulphuryl chloride is

[CPMT 1992]

(a) 0.1 (b) 0.2

(c) 0.3 (d) 0.4

20. The largest number of molecules is in **[BHU 1997]**

(a) $34g$ of water (b) $28g$ of CO_2

(c) $46g$ of CH_3OH (d) $54g$ of N_2O_5

21. The number of moles of sodium oxide in $620g$ of it is

[BHU 1992]

(a) 1 mol (b) 10 moles

(c) 18 moles (d) 100 moles

22. $2g$ of oxygen contains number of atoms equal to that in

[BHU 1992]

(a) $0.5g$ of hydrogen (b) $4g$ of sulphur

(c) $7g$ of nitrogen (d) $2.3g$ of sodium

23. Molarity of liquid HCl with density equal to $1.17g/cc$ is

[CBSE PMT 2001]

(a) 36.5 (b) 18.25

(c) 32.05 (d) 4.65

24. How many atoms are contained in one mole of sucrose $(C_{12}H_{22}O_{11})$ **[Pb. PMT 2002]**

(a) $45 \times 6.02 \times 10^{23}$ atoms/mole

(b) $5 \times 6.62 \times 10^{23}$ atoms/mole

(c) $5 \times 6.02 \times 10^{23}$ atoms/mole

(d) None of these

25. The number of molecules of CO_2 present in 44*g* of CO_2 is **[BCECE 2005]**

(a) 6.0×10^{23} (b) 3×10^{23}

(c) 12×10^{23} (d) 3×10^{10}

26. A sample of phosphorus trichloride (PCl_3) contains 1.4 moles of the substance. How many atoms are there in the sample **[Kerala PMT 2004]**

(a) 4 (b) 5.6

(c) 8.431×10^{23} (d) 3.372×10^{24}

(e) 2.409×10^{24}

27. The number of sodium atoms in 2 moles of sodium ferrocyanide is **[BHU 2004]**

(a) 12×10^{23} (b) 26×10^{23}

(c) 34×10^{23} (d) 48×10^{23}

Percentage composition & Molecular formula

1. The percentage of oxygen in $NaOH$ is **[CPMT 1979]**

(a) 40 (b) 60

(c) 8 (d) 10

2. The percentage of nitrogen in urea is about **[KCET 2001]**

(a) 46 (b) 85

(c) 18 (d) 28

3. If two compounds have the same empirical formula but different molecular formula, they must have **[MP PMT 1986]**

(a) Different percentage composition

(b) Different molecular weights

(c) Same viscosity

(d) Same vapour density

4. A compound (80 *g*) on analysis gave *C* = 24 g, *H* = 4 *g*, *O* = 32 *g*. Its empirical formula is **[CPMT 1981]**

(a) $C_2H_2O_2$ (b) C_2H_2O

(c) CH_2O_2 (d) CH_2O

5. The empirical formula of a compound is CH_2O. 0.0835 moles of the compound contains 1.0 *g* of hydrogen. Molecular formula of the compound is

(a) $C_2H_{12}O_6$ (b) $C_5H_{10}O_5$

(c) $C_4H_8O_8$ (d) $C_3H_6O_3$

6. The empirical formula of an acid is CH_2O_2, the probable molecular formula of acid may be **[AFMC 2000]**

(a) CH_2O (b) CH_2O_2

(c) $C_2H_4O_2$ (d) $C_3H_6O_4$

7. In which of the following pairs of compounds the ratio of *C, H* and *O* is same

(a) Acetic acid and methyl alcohol

(b) Glucose and acetic acid

(c) Fructose and sucrose

(d) All of these

Chemical stoichiometry

1. How much of *NaOH* is required to neutralise 1500 cm^3 of 0.1 $N\ HCl$ (*Na* = 23) **[KCET 2001]**

(a) 40 *g* (b) 4 *g*

(c) 6 *g* (d) 60 *g*

2. How much water should be added to 200 c.c of semi normal solution of $NaOH$ to make it exactly deci normal **[AFMC 1983]**

(a) 200 *cc* (b) 400 *cc*

(c) 800 *cc* (d) 600 *cc*

3. 2.76 *g* of silver carbonate on being strongly heated yield a residue weighing **[Pb. CET 2003]**

(a) 2.16 *g* (b) 2.48 *g*

(c) 2.64 *g* (d) 2.32 *g*

4. In the reaction, $4NH_3(g)+5O_2(g)\rightarrow4NO(g)+6H_2O(g)$, When 1 mole of ammonia and 1 mole of O_2 are made to react to completion

(a) 1.0 mole of H_2O is produced

(b) 1.0 mole of NO will be produced

(c) All the oxygen will be consumed

(d) All the ammonia will be consumed

5. Haemoglobin contains 0.33% of iron by weight. The molecular weight of haemoglobin is approximately 67200. The number of iron atoms (At. wt. of *Fe* = 56) present in one molecule of haemoglobin is **[CBSE PMT 1998]**

(a) 6 (b) 1

(c) 4 (d) 2

6. What quantity of ammonium sulphate is necessary for the production of NH_3 gas sufficient to neutralize a solution containing 292 g of HCl ? [HCl=36.5; $(NH_4)_2SO_4$ =132; NH_3 =17]

[CPMT 1992]

(a) 272 g
(b) 403 g
(c) 528 g
(d) 1056 g

7. The percentage of P_2O_5 in diammonium hydrogen phosphate $(NH_4)_2HPO_4$ is

[CPMT 1992]

(a) 23.48
(b) 46.96
(c) 53.78
(d) 71.00

8. If $1\frac{1}{2}$ moles of oxygen combine with Al to form Al_2O_3 the weight of Al used in the reaction is (Al=27)

[EAMCET 1980]

(a) 27 g
(b) 54 g
(c) 49.5 g
(d) 31 g

9. The percentage of *Se* in peroxidase anhydrous enzyme is 0.5% by weight (atomic weight=78.4). Then minimum molecular weight of peroxidase anhydrous enzyme is

[CBSE PMT 2001]

(a) 1.568×10^4
(b) 1.568×10^3
(c) 15.68
(d) 3.136×10^4

10. H_2 evolved at STP on complete reaction of 27 g of Aluminium with excess of aqueous $NaOH$ would be

[CPMT 1991]

(a) 22.4
(b) 44.8
(c) 67.2
(d) 33.6 *litres*

11. What is the % of H_2O in $Fe(CNS)_3.3H_2O$

(a) 45
(b) 30
(c) 19
(d) 25

12. What weight of SO_2 can be made by burning sulphur in 5.0 moles of oxygen

(a) 640 *grams*
(b) 160 *grams*
(c) 80 *grams*
(d) 320 *grams*

13. What is the normality of a 1 M solution of H_3PO_4

[AIIMS 1982]

(a) 0.5 N
(b) 1.0 N
(c) 2.0 N
(d) 3.0 N

14. Normality of 2M sulphuric acid is

[AIIMS 1992]

(a) 2N
(b) 4N
(c) $\frac{N}{2}$
(d) $\frac{N}{4}$

15. How many g of a dibasic acid (Mol. wt. = 200) should be present in 100 *ml* of its aqueous solution to give decinormal strength **[AIIMS 1992]**

(a) 1 g
(b) 2 g
(c) 10 g
(d) 20 g

16. The solution of sulphuric acid contains 80% by weight H_2SO_4. Specific gravity of this solution is 1.71. Its normality is about **[CBSE 1991]**

(a) 18.0
(b) 27.9
(c) 1.0
(d) 10.0

17. Mohr's salt is dissolved in dil. H_2SO_4 instead of distilled water to

(a) Enhance the rate of dissolution
(b) Prevent cationic hydrolysis
(c) Increase the rate of ionisation
(d) Increase its reducing strength

18. Acidified potassium permanganate solution is decolourised by

[MNR 1984]

(a) Bleaching powder
(b) White vitriol
(c) Mohr's salt
(d) Microcosmic salt

19. Approximate atomic weight of an element is 26.89. If its equivalent weight is 8.9, the exact atomic weight of element would be **[DPMT 1984]**

(a) 26.89
(b) 8.9
(c) 17.8
(d) 26.7

20. Vapour density of a gas is 22. What is its molecular mass

[AFMC 2000]

(a) 33
(b) 22
(c) 44
(d) 11

21. Equivalent weight of $KMnO_4$ acting as an oxidant in acidic medium is **[CPMT 1990; MP PET 1999]**

(a) The same as its molecular weight
(b) Half of its molecular weight
(c) One-third of its molecular weight
(d) One-fifth of its molecular weight

22. 0.16 *g* of dibasic acid required 25 *ml* of decinormal *NaOH* solution for complete neutralisation. The molecular weight of the acid will be

[CPMT 1989]

(a) 32 (b) 64

(c) 128 (d) 256

23. To neutralise 20 *ml* of $M/10$ sodium hydroxide, the volume of $M/20$ hydrochloric acid required is

[Andhra MBBS 1980]

(a) 10 *ml* (b) 15 *ml*

(c) 20 *ml* (d) 40 *ml*

24. Hydrochloric acid solutions *A* and *B* have concentration of 0.5 *N* and 0.1 *N* respectively. The volume of solutions *A* and *B* required to make 2 *litres* of 0.2 *N* hydrochloric are

[KCET 1993]

(a) 0.5 *l* of *A* + 1.5 *l* of *B*

(b) 1.5 *l* of *A* + 0.5 *l* of *B*

(c) 1.0 *l* of *A* + 1.0 *l* of *B*

(d) 0.75 *l* of *A* + 1.25 *l* of *B*

25. 5 *ml* of *N HCl*, 20 *ml* of $N/2\ H_2SO_4$ and 30 *ml* of $N/3\ HNO_3$ are mixed together and volume made to one *litre*. The normality of the resulting solution is **[MNR 1991]**

(a) $N/5$ (b) $N/10$

(c) $N/20$ (d) $N/40$

26. Under similar conditions of pressure and temperature, 40 *ml* of slightly moist hydrogen chloride gas is mixed with 20 *ml* of ammonia gas, the final volume of gas at the same temperature and pressure will be **[CBSE PMT 1993]**

(a) 100 *ml* (b) 20 *ml*

(c) 40 *ml* (d) 60 *ml*

27. $KMnO_4$ reacts with oxalic acid according to the equation,

$$2MnO_4^- + 5C_2O_4^{2-} + 16H^+ \rightarrow 2Mn^{2+} + 10CO_2 + 8H$$

, here 20 *ml* of 0.1 *M* $KMnO_4$ is equivalent to **[CBSE PMT 1996]**

(a) 20 *ml* of 0.5 *M* $H_2C_2O_4$ (b) 50 *ml* of 0.1 *M* $H_2C_2O_4$

(c) 50 *ml* of 0.5 *M* $H_2C_2O_4$ (d) 20 *ml* of 0.1 *M* $H_2C_2O_4$

28. In order to prepare one *litre* normal solution of $KMnO_4$, how many *grams* of $KMnO_4$ are required if the solution is used in acidic medium for oxidation **[MP PET 2002]**

(a) 158 *g* (b) 31.6 *g*

(c) 790 *g* (d) 62 *g*

29. What is the concentration of nitrate ions if equal volumes of 0.1 *M* $AgNO_3$ and 0.1 *M NaCl* are mixed together

[NCERT 1981; CPMT 1983]

(a) 0.1 *N* (b) 0.2 *M*

(c) 0.05 *M* (d) 0.25 *M*

30. 30 *ml* of acid solution is neutralized by 15 *ml* of a 0.2 *N* base. The strength of acid solution is **[CPMT 1986]**

(a) 0.1 *N* (b) 0.15 *N*

(c) 0.3 *N* (d) 0.4 *N*

31. A solution containing Na_2CO_3 and *NaOH* requires 300 *ml* of 0.1 *N HCl* using phenolpthalein as an indicator. Methyl orange is then added to the above titrated solution when a further 25 *ml* of 0.2 *N HCl* is required. The amount of *NaOH* present in solution is $(NaOH = 40, Na_2CO_3 = 106)$

[CPMT 1992]

(a) 0.6 *g* (b) 1.0 *g*

(c) 1.5 *g* (d) 2.0 *g*

32. In the preceeding question, the amount of Na_2CO_3 present in the solution is **[CPMT 1992]**

(a) 2.650 *g* (b) 1.060 *g*

(c) 0.530 *g* (d) 0.265 *g*

33. How many *ml* of 1 (*M*) H_2SO_4 is required to neutralise 10 *ml* of 1 (*M*) *NaOH* solution

[MP PET 1998; MNR 1982; MP PMT 1987]

(a) 2.5 (b) 5.0

(c) 10.0 (d) 20.0

34. Which of the following cannot give iodometric titrations

[AIIMS 1997]

(a) Fe^{3+} (b) Cu^{2+}

(c) Pb^{2+} (d) Ag^+

35. $KMnO_4$ reacts with ferrous ammonium sulphate according to the equation

$$MnO_4^- + 5Fe^{2+} + 8H^+ \rightarrow Mn^{2+} + 5Fe^{3+} + 4H_2O,$$

here 10 *ml* of 0.1 *M* $KMnO_4$ is equivalent to **[CPMT 1999]**

(a) 20 *ml* of 0.1 *M* $FeSO_4$

(b) 30 *ml* of 0.1 *M* $FeSO_4$

(c) 40 *ml* of 0.1 *M* $FeSO_4$

(d) 50 *ml* of 0.1 *M* $FeSO_4$

36. $Ca(OH)_2 + H_3PO_4 \rightarrow CaHPO_4 + 2H_2O$ the equivalent weight of H_3PO_4 in the above reaction is **[Pb. PMT 2004]**

(a) 21 (b) 27

(c) 38 (d) 49

37. The mass of $BaCO_3$ produced when excess CO_2 is bubbled through a solution of 0.205 mol $Ba(OH)_2$ is **[UPSEAT 2004]**

(a) 81 *g* (b) 40.5 *g*

(c) 20.25 *g* (d) 162 *g*

38. The amount of water that should be added to 500 *ml* of 0.5 *N* solution of $NaOH$ to give a concentration of 10 *mg* per *ml* is

(a) 100 (b) 200

(c) 250 (d) 500

39. Number of moles of $KMnO_4$ required to oxidize one mole of $Fe(C_2O_4)$ in acidic medium is **[Haryana CEE 1996]**

(a) 0.6 (b) 0.167

(c) 0.2 (d) 0.4

40. A hydrocarbon contains 86% carbon, 488ml of the hydrocarbon weight 1.68 *g* at STP. Then the hydrocarbon is an

(a) Alkane (b) Alkene

(c) Alkyne (d) Arene

41. The ratio of amounts of H_2S needed to precipitate all the metal ions from 100 *ml* of 1 *M* $AgNO_3$ and 100 *ml* of 1 *M* $CuSO_4$ will be

(a) 1:1 (b) 1:2

(c) 2:1 (d) None of these

42. An electric discharge is passed through a mixture containing 50 *c.c.* of O_2 and 50 *c.c.* of H_2. The volume of the gases formed (i) at room temperature and (ii) at 110^0C will be

(a) (i) 25 *c.c.* (ii) 50 *c.c.* (b) (i) 50 *c.c.* (ii) 75 *c.c.*

(c) (i) 25 *c.c.* (ii) 75 *c.c.* (d) (i) 75 *c.c.* (ii) 75 *c.c.*

43. 100 *ml* of 0.1 *N* hypo decolourised iodine by the addition of *x g* of crystalline copper sulphate to excess of *KI*. The value of '*x*' is (molecular wt. of $CuSO_4.5H_2O$ is 250)

(a) 5.0 *g* (b) 1.25 *g*

(c) 2.5 *g* (d) 4 *g*

44. How many grams of caustic potash required to completely neutralise 12.6 *gm* HNO_3

(a) 22.4 *KOH* (b) 1.01 *KOH*

(c) 6.02 *KOH* (d) 11.2 *KOH*

45. If isobutane and n-butane are present in a gas, then how much oxygen should be required for complete combustion of 5 *kg* of this gas

(a) 17.9 *kg* (b) 9 *kg*

(c) 27 *kg* (d) 1.8 *kg*

46. 16.8 *litre* gas containing H_2 and O_2 is formed at NTP on electrolysis of water. What should be the weight of electrolysed water

(a) 5 *g* (b) 9 *g*

(c) 10 *g* (d) 12 *g*

47. On electrical decomposition of 150 *ml* dry and pure O_2, 10% of O_2 gets changed to *O*, then the volume of gaseous mixture after reaction and volume of remaining gas left after passing in turpentine oil will be

(a) 145 *ml* (b) 149 *ml*

(c) 128 *ml* (d) 125 *ml*

48. What should be the weight of 50% *HCl* which reacts with 100 *g* of limestone

(a) 50% pure (b) 25% pure

(c) 10% pure (d) 8% pure

49. What should be the weight and moles of $AgCl$ precipitate obtained on adding 500ml of 0.20 *M* HCl in 30 *g* of $AgNO_3$ solution? ($AgNO_3$ = 170)

(a) 14.35 *g* (b) 15 *g*

(c) 18 *g* (d) 19 *g*

50. A solution of 10 *ml* $\frac{M}{10} FeSO_4$ was titrated with $KMnO_4$ solution in acidic medium. The amount of $KMnO_4$ used will be **[CPMT 1984]**

(a) 5 *ml* of 0.1 *M* (b) 10 *ml* of 1.1 *M*

(c) 10 *ml* of 0.5 *M* (d) 10 *ml* of 0.02 *M*

51. 1.12 *ml* of a gas is produced at STP by the action of 4.12 *mg* of alcohol, with methyl magnesium iodide. The molecular mass of alcohol is

[Roorkee 1992; IIT 1993]

(a) 16.0 (b) 41.2

(c) 82.4 (d) 156.0

52. The simplest formula of a compound containing 50% of element X (atomic mass 10) and 50% of element *Y* (atomic mass 20) is **[Roorkee 1994]**

(a) XY (b) X_2Y

(c) XY_3 (d) X_2Y_3

53. A compound contains atoms of three elements in *A, B* and *C*. If the oxidation number of *A* is +2, *B* is +5 and that of *C* is – 2, the possible formula of the compound is

[CBSE PMT 2000]

(a) $A_3(BC_4)_2$

(b) $A_3(B_4C)_2$

(c) ABC_2

(d) $A_2(BC_3)_2$

54. What will be the volume of CO_2 at NTP obtained on heating 10 grams of (90% pure) limestone **[Pb. CET 2001]**

(a) 22.4 *litre*

(b) 2.016 *litre*

(c) 2.24 *litre*

(d) 20.16 *litre*

55. The ratio of the molar amounts of H_2S needed to precipitate the metal ions from $20 mL$ each of $1M\ Cd(NO_3)_2$ and $0.5M\ CuSO_4$ is **[CPMT 1997]**

(a) 1 : 1

(b) 2 : 1

(c) 1 : 2

(d) Indefinite

56. $12g$ of Mg (at. mass 24) will react completely with acid to give **[MNR 1985]**

(a) One mole of H_2

(b) 1/2 mole of H_2

(c) 2/3 mole of O_2

(d) Both 1/2 mol of H_2 and 1/2 mol of O_2

57. 1.5 *mol* of O_2 combine with Mg to form oxide MgO. The mass of Mg (at. mass 24) that has combined is

[KCET 2001]

(a) $72\ g$ (b) $36\ g$

(c) $48\ g$ (d) $24\ g$

58. 100 *g* $CaCO_3$ reacts with 1*litre* 1 *N HCl*. On completion of reaction how much weight of CO_2 will be obtain

[Kerala CET 2005]

(a) $5.5\ g$ (b) $11\ g$

(c) $22\ g$ (d) $33\ g$

(e) $44\ g$

Critical Thinking

Objective Questions

1. Mixture of sand and sulphur may best be separated by

[Kerala CET 2001]

(a) Fractional crystallisation from aqueous solution

(b) Magnetic method

(c) Fractional distillation

(d) Dissolving in CS_2 and filtering

2. Irrespective of the source, pure sample of water always yields 88.89% mass of oxygen and 11.11% mass of hydrogen. This is explained by the law of

[Kerala CEE 2002]

(a) Conservation of mass (b) Constant composition

(c) Multiple proportions (d) Constant volume

3. Zinc sulphate contains 22.65% of zinc and 43.9% of water of crystallization. If the law of constant proportions is true, then the weight of zinc required to produce 20 *g* of the crystals will be

(a) 45.3 *g* (b) 4.53 *g*

(c) 0.453 *g* (d) 453 *g*

4. 10 dm^3 of N_2 gas and 10 dm^3 of gas *X* at the same temperature contain the same number of molecules. The gas *X* is

(a) CO
(b) CO_2
(c) H_2
(d) *NO*

5. The molar heat capacity of water at constant pressure is 75 $JK^{-1}\ mol^{-1}$. When 1.0 *kJ* of heat is supplied to 100 *g* of water which is free to expand, the increases in temperature of water is **[CBSE PMT 2003]**

(a) 6.6 *K*
(b) 1.2 *K*
(c) 2.4 *K*
(d) 4.8 *K*

6. A compound possesses 8% sulphur by mass. The least molecular mass is **[AIIMS 2002]**

(a) 200
(b) 400
(c) 155
(d) 355

7. Which of the following contains maximum number of atoms

[JIPMER 2000]

(a) 6.023×10^{21} molecules of CO_2
(b) 22.4 *L* of CO_2 at STP
(c) 0.44 *g* of CO_2
(d) None of these

8. In a mole of water vapour at STP, the volume actually occupied or taken by the molecules (i.e., Avogadro's No. × Volume of one molecule) is **[Kerala EEE 2000]**

(a) Zero
(b) Less than 1% of 22.4 litres
(c) About 10% of the volume of container
(d) 1% to 2% of 22.4 litres
(e) Between 2% to 5% of 22.4 litres

9. If 10^{21} molecules are removed from 200*mg* of CO_2, then the number of moles of CO_2 left are **[IIT 1983]**

(a) 2.85×10^{-3}
(b) 28.8×10^{-3}
(c) 0.288×10^{-3}
(d) 1.68×10^{-2}

10. The set of numerical coefficient that balances the equation $K_2CrO_4 + HCl \rightarrow K_2Cr_2O_7 + KCl + H_2O$ is

[Kerala CEE 2001]

(a) 1, 1, 2, 2, 1
(b) 2, 2, 1, 1, 1
(c) 2, 1, 1, 2, 1
(d) 2, 2, 1, 2, 1

11. One litre hard water contains 12.00 *mg* Mg^{2+} milli equivalent of washing soda required to remove its hardness is

[CBSE PMT 2001]

(a) 1
(b) 12.15
(c) 1×10^{-3}
(d) 12.15×10^{-3}

12. In standardization of $Na_2S_2O_3$ using $K_2Cr_2O_7$ by iodometry, the equivalent weight of $K_2Cr_2O_7$ is **[IIT 2000]**

(a) $MW/2$
(b) $MW/3$
(c) $MW/6$
(d) $MW/1$

13. 3.92 *g* of ferrous ammonium sulphate crystals are dissolved in 100 *ml* of water, 20 *ml* of this solution requires 18 *ml* of $KMnO_4$ during titration for complete oxidation. The weight of $KMnO_4$ present in one *litre* of the solution is

[Tamilnadu CET 2002]

(a) 3.476 *g*
(b) 12.38 *g*
(c) 34.76 *g*
(d) 1.238 *g*

14. A 100 *ml* solution of 0.1 *n HCl* was titrated with 0.2 *N NaOH* solution. The titration was discontinued after adding 30 *ml* of *NaOH* solution. The remaining titration was completed by adding 0.25 *N KOH* solution. The volume of *KOH* required for completing the titration is **[DCE 1999]**

(a) 70 *ml*
(b) 32 *ml*
(c) 35 *ml*
(d) 16 *ml*

15. What volume of Hydrogen gas, at 273 *K* and 1 atm pressure will be consumed in obtaining 21.6 *g* of elemental boron (atomic mass = 10.8) from the reduction of boron trichloride by Hydrogen

[AIEEE 2003]

(a) 22.4 *L*
(b) 89.6 *L*
(c) 67.2 *L*
(d) 44.8 *L*

16. The mass of $112\ cm^3$ of CH_4 gas at STP is

[Karnataka CET 2001]

(a) $0.16\ g$
(b) $0.8\ g$
(c) $0.08\ g$
(d) $1.6\ g$

17. Complete combustion of $0.858\ g$ of compound *X* gives $2.63\ g$ of CO_2 and $1.28\ g$ of H_2O. The lowest molecular mass *X* can have

[Kerala MEE 2000]

(a) $43\ g$
(b) $86\ g$
(c) $129\ g$
(d) $172\ g$

18. In the following reaction, which choice has value twice that of the equivalent mass of the oxidising agent

$SO_2 + H_2O \longrightarrow 3S + 2H_2O$ **[DPMT 2000]**

(a) 64
(b) 32

(c) 16 (d) 48

Assertion & Reason

For AIIMS Aspirants

Read the assertion and reason carefully to mark the correct option out of the options given below :

- *(a) If both assertion and reason are true and the reason is the correct explanation of the assertion.*
- *(b) If both assertion and reason are true but reason is not the correct explanation of the assertion.*
- *(c) If assertion is true but reason is false.*
- *(d) If the assertion and reason both are false.*
- *(e) If assertion is false but reason is true.*

1. Assertion : Volume of a gas is inversely proportional to the number of moles of a gas.

Reason : The ratio by volume of gaseous reactants and products is in agreement with their mole ratio.

[AIIMS 1995]

2. Assertion : Molecular weight of oxygen is 16.

Reason : Atomic weight of oxygen is 16.

[AIIMS 1996]

3. Assertion : Atoms can neither be created nor destroyed.

Reason : Under similar condition of temperature and pressure, equal volume of gases does not contain equal number of atoms.

[AIIMS 1994,2002]

4. Assertion : One mole of SO_2 contains double the number of molecules present in one mole of O_2.

Reason : Molecular weight of SO_2 is double to that of O_2.

5. Assertion : 1.231 has three significant figures.

Reason : All numbers right to the decimal point are significant.

6. Assertion : 22.4 *L* of N_2 at NTP and 5.6 *L* O_2 at NTP contain equal number of molecules.

Reason : Under similar conditions of temperature and pressure all gases contain equal number of molecules.

7. Assertion : One atomic mass unit (amu) is mass of an atom equal to exactly one-twelfth the mass of a carbon-12 atom.

Reason : Carbon-12 isotope was selected as standard.

8. Assertion : Molecular mass of *A* is $\frac{M}{4}$ if the molecular mass of *B* is *M*.

Reason : Vapour density of *A* four times that of *B*.

9. Assertion : Pure water obtained from different sources such as, river, well, spring, sea etc. always contains hydrogen and oxygen combined in the ratio $1:8$ by mass.

Reason : A chemical compound always contains elements combined together in same proportion by mass, it was discovered by French chemist, Joseph Proust (1799).

10. Assertion : As mole is the basic chemical unit, the concentration of the dissolved solute is usually specified in terms of number of moles of solute.

Reason : The total number of molecules of reactants involved in a balanced chemical equation is known as molecularity of the reaction.

11. Assertion : A certain element *X*, forms three binary compounds with chlorine containing 59.68%,68.95% and 74.75% chlorine respectively. These data illustrate the law of multiple proportions.

Reason : According to law of multiple proportions, the relative amounts of an element combining with some fixed amount of a second element in a series of compounds are the ratios of small whole numbers.

12. Assertion : Equivalent weight of Cu in CuO is 63.6 and in Cu_2O 31.8.

Reason : Equivalent weight of an element

$$=\frac{\text{Atomic weight of the element}}{\text{Valency of the element}}$$

13. Assertion : Mass spectrometer is used for the determination of isotopes.

Reason : Isotopes are the atoms of same element differing in mass numbers.

14. Assertion : Gases combine in simple ratio of their volume but, not always.

Reason : Gases deviate from ideal behaviour.

15. Assertion : Isomorphous substances form crystals of same shape and can grow in saturated solution of each other.

Reason : They have similar constitution and chemical formulae.

16. Assertion : Atomicity of oxygen is 2.

Reason : 1 mole of an element contains 6.023×10^{23} atoms.

17. Assertion : 1 amu equals to $1.66\times10^{-24}\ g$.

Reason : $1.66\times10^{-24}\ g$ equals to $\frac{1}{12}th$ of mass of a C^{12} atom.

Answers

Significant figures, Units for measurement, Matter and Separation of mixture

1	a	2	d	3	a	4	c	5	d
6	b	7	c	8	d	9	c	10	c
11	c	12	b	13	a	14	c	15	b
16	b	17	b	18	a	19	a	20	c
21	b	22	d	23	a	24	a	25	b
26	b	27	d						

Laws of chemical combination

1	a	2	d	3	c	4	a	5	c
6	c	7	c	8	b	9	b	10	a
11	c	12	b	13	a	14	d	15	b
16	a	17	c	18	d	19	c	20	a
21	c	22	d						

Atomic, Molecular and Equivalent masses

1	c	2	b	3	a	4	a	5	b
6	c	7	d	8	b	9	a	10	b
11	a	12	b	13	a	14	c	15	b
16	c	17	a	18	d	19	a	20	a
21	b	22	b	23	d	24	c	25	a
26	a	27	c	28	d	29	a	30	c
31	a	32	d	33	b	34	a	35	c
36	b	37	b	38	c	39	a	40	b
41	c	42	d	43	a	44	d	45	d
46	b	47	c	48	c	49	b	50	b
51	a	52	b	53	b	54	c	55	b
56	a	57	d	58	d	59	a	60	d
61	c	62	d	63	b				

The mole concept

1	a	2	b	3	b	4	c	5	a
6	b	7	a	8	c	9	d	10	c
11	b	12	c	13	c	14	d	15	a
16	a	17	b	18	b	19	a	20	a
21	b	22	b	23	c	24	a	25	a
26	c	27	d						

Percentage composition & Molecular formula

1	a	2	a	3	b	4	d	5	a
6	b	7	b						

Chemical stoichiometry

1	c	2	c	3	a	4	c	5	c
6	c	7	c	8	b	9	a	10	d
11	c	12	d	13	d	14	b	15	a
16	b	17	b	18	c	19	d	20	c
21	d	22	c	23	d	24	a	25	d
26	b	27	b	28	b	29	c	30	a
31	b	32	c	33	b	34	c	35	d
36	d	37	b	38	d	39	a	40	b
41	b	42	c	43	c	44	d	45	a
46	b	47	a	48	a	49	a	50	d
51	c	52	b	53	a	54	b	55	b
56	b	57	a	58	c				

Critical Thinking Questions

1	d	2	b	3	b	4	a	5	c
6	b	7	b	8	b	9	a	10	d
11	a	12	c	13	a	14	d	15	c
16	c	17	a	18	b				

Assertion & Reason

1	e	2	e	3	c	4	e	5	d
6	d	7	a	8	c	9	a	10	b
11	a	12	e	13	e	14	a	15	a
16	b	17	a						

Answers and Solutions

Significant figures, Units of measurement, Matter and Separation of mixture

4. (c) Pressure $= \frac{\text{Force}}{\text{Area}} = \frac{[MLT^{-2}]}{[L^2]} = [ML^{-1}T^{-2}]$

Energy per unit volume $= \frac{[ML^2T^{-2}]}{[L^3]} = [ML^{-1}T^{-2}]$

17. (b) $\frac{(29.2-20.2)(1.79\times10^5)}{1.37}$

$= \frac{9.0\times1.79\times10^5}{1.37}$

Least precise terms *i.e.,* 9.0 has only two significant figures. Hence, final answer will have two significant figures.

18. (a) Pure ethyl alcohol $= 81.4 - 0.002 = 81.398$.

19. (a) *JPa*$^{-1}$; Unit of work is *Joule* and unit of pressure is *Pascal*.

Dimension of *Joule* *i.e.* work $= F\times L$

$= MLT^{-2}\times L$

$= \left[ML^2T^{-2}\right]$

$$\frac{1}{Pa} = \frac{1}{\text{Pressure}} = \frac{1}{\frac{F}{A}} = \frac{1\times A}{F} = \left[MLT^{-1}\right]$$

So, JPa^{-1} $= \left[ML^2T^2\right] = \left[L^2\times L\right] = \left[L^3\right]$.

22. (d) 1 zepto $= 10^{-21}$

23. (a) As we know that all non zero unit are significant number. Therefore significant figure is 2.

24. (a) Number of significant figures in 6.0023 are 5 because all the zeroes stand between two non zero digit are counted towards significant figures.

25. (b) Given $P = 0.0030m$, $Q = 2.40m$ & $R = 3000m$ In $P(0.0030)$ initial zeros after the decimal point are not significant. Therefore, significant figures in $P(0.0030)$ are 2. Similarly in $Q(2.40)$ significant figures are 3 as in this case final zero is significant. In $R = (3000)$ all the zeroes are significant hence, in R significant figures are 4.

26. (b) All the zeroes between two non zero digit are significatn. Hence in 60.0001 significant figures is 6.

27. (d) Round off the digit at 2nd position of decimal 3.929 = 3.93.

Laws of chemical combination

12. (b) $\underset{ng}{X} + \underset{mg}{Y} \rightleftharpoons \underset{pg}{R} + \underset{qg}{S}$

$n+m = p+q$ by low of conservation of mass.

Atomic, Molecular and Equivalent masses

5. (b) The atomic weight of sulphur =32

In SCl_2 valency of sulphur =2

So equivalent mass of sulphur $= \frac{32}{2} = 16$.

6. (c) As the given sulphate is isomorphous with $ZnSO_4.7H_2O$ its formula would be $MSO_4.7H_2O$.*m* is the atomic weight of *M*, molecular weight of $MSO_4.7H_2O$ $= m+32+64+126$ $= m+222$

Hence % of $M = \frac{m}{m+222}\times100 = 9.87$ (given) or

$100m = 9.87m + 222\times9.87$ or

$90.13m = 222\times9.87$

or $m = \frac{222\times9.87}{90.13} = 24.3$.

7. (d) For *NaOH*, $M = N$

$N_1V_1 = 100ml \times 1N = 100ml(N)$

For H_2SO_4, $N_2V_2 = 10ml \times 10N = 100ml(N)$

Hence, $N_1V_1 = N_2V_2$.

10. (b) 1 mole of CH_4 contains 4 mole of hydrogen atom *i.e.* 4*g* atom of hydrogen.

11. (a) $Na_2\overset{+2}{S}O_3 + I_2 \rightarrow Na_2\overset{+2.5}{S}_4O_6 + NaI$

$n = 2 \times 0.5 = 1$

$E = \frac{M}{n-\text{factor}} = \frac{M}{1} = M$

12. (b) $E = \frac{M}{5}$

13. (a) Atomic mass $= \frac{10 \times 19 + 81 \times 11}{100} = \frac{190 + 891}{100}$

$= \frac{1081}{100}$

$= 10.81$

14. (c) 0.1*M* $AgNO_3$ will react with 0.1*M* *NaCl* to form $0.1M\ NaNO_3$. But as the volume doubled, conc. of $NO_3^- = \frac{0.1}{2} = 0.05M$.

16. (c) wt. of metallic chloride $= 74.5$

wt. of chlorine = 35.5

$\therefore$ wt. of metal $= 74.5 - 35.5 = 39$

Equivalent weight of metal $= \frac{\text{weight of metal}}{\text{weight of chlorine}} \times 35.5$

$= \frac{39}{35.5} \times 35.5 = 39$

17. (a) $\because$ 5.8*L* of gas has mass $= 7.5gm$

$\therefore$ 22.4*L* " " " $= \frac{7.5}{5.8} \times 22.4 = 28.96$

So molecular weight = 29

So, molecular formula of compound is *NO*

18. (d) $\because$ 17*gm* NH_3 contains 6×10^{23} molecules of NH_3

$\therefore$ 4.25*gm* NH_3 contains = $\frac{6 \times 10^{23}}{17} \times 4.25$

$\therefore$ No. of atoms $= \frac{6 \times 10^{23} \times 4.25}{17} \times 4$

$= 6 \times 10^{23}$.

19. (a) $\because$ 1*L* of gas at S.T.P. weight 1.16*g*

$\therefore$ 22.4 *L* of gas at S.T.P. weight $= 22.4 \times 1.16$

$= 25.984 \approx 26$

This molecular weight indicates that given compound is C_2H_2.

20. (a) Molecular weight $= 2 \times V.D = 2 \times 11.2 = 22.4$

$\because$ 22.4*gm* of gas occupies 22.4*L* at S.T.P.

$\therefore$ 11.2*gm* of gas occupies

$\frac{22.4}{22.4} \times 11.2 = 11.2L$.

21. (b) Equivalent weight $= \frac{\text{Molecular weight}}{\text{Valency}}$

Molecular weight of $\begin{array}{l} COOH \\ | \\ COOH \end{array} \cdot 2H_2O = \frac{126}{2} = 63$

.

22. (b) Valency of the element $= \frac{2 \times V.D}{E + 35.5} = \frac{2 \times 59.25}{4 + 35.5}$

$= \frac{118.50}{39.5}$ =3.

23. (d) Molarity $= \frac{W(gm) \times 1000}{V(ml) \times \text{molecular weight}}$

$0.25 = \frac{1.25 \times 1000}{25 \times \text{molecular weight}}$

$\therefore$ Molecular weight $= \frac{1.25 \times 1000}{0.25 \times 25} = 200$.

24. (c) Let weight of metal oxide = 100*gm*

Weight of oxygen = 32*gm*

$\therefore$ weight of metal $= 100 - 32 = 68gm$

Equivalent weight of oxide

$= \frac{\text{wt. of metal}}{\text{wt. of oxygen}} \times 8$

$= \frac{68}{32} \times 8 = 17$.

25. (a) 6×10^{23} molecules has mass $= 18gm$

1 molecules has mass $= \frac{18}{6 \times 10^{23}}$

$= 3 \times 10^{-23} gm$

$= 3 \times 10^{-26} kg$.

26. (a) Choice (a) is P_4S_3

$\because$ $\frac{31\times 4}{(124)}\,gm\,P$ is present in 220*gm* P_4S_3

$\therefore$ 1.24*gm P* is present in =

$\frac{220}{124}\times 1.24 = 2.2gm$

27. (c) Number of moles of $A=\frac{x}{40}$

Number of atoms of *A*

$=\frac{x}{40}\times \text{Avogadro no.} = y$ (say)

Or $x=\frac{40y}{\text{Avogadro no.}}$

Number of moles of $B=\frac{2x}{80}$

Number of atoms of *B*

$=\frac{2x}{80}\times \text{Av. no.} = \frac{2}{80}\times\frac{40y}{\text{Av. no.}}\times \text{Av. no.} = y$

28. (d) $BaCO_3 \to BaO + CO_2\uparrow$

Molecular weight of $BaCO_3 = 137+12+3\times 16$ =197

$\because$ 197*gm* produces 22.4*L* at S.T.P.

$\therefore$ 9.85*gm* produces $\frac{22.4}{197}\times 9.85 = 1.12L$ at S.T.P.

29. (a) 14 *gm* N^{3-} ions have $=8N_A$ valence electrons

4.2*gm* of N^{3-} ions have

$=\frac{8N_A\times 4.2}{14}=2.4N_A$

30. (c) [$\because$ Molecular weight of $CuSO_4.5H_2O$

$=63.5+32+64+90 = 249.5$]

6×10^{23} molecules has weight $=249.5gm$

1×10^{22} molecules has weight

$=\frac{249.5\times 1\times 10^{22}}{6\times 10^{23}}$

$=41.58\times 10^{-1}$

$=4.158$

31. (a) (I) 1 molecule of oxygen

$\because$ 6×10^{23} molecule has mass $=32gm$

$\therefore$ 1 molecule of O_2 has mass $=\frac{32}{6\times 10^{23}}$

$=5.3\times 10^{-23}gm$

(II) 1 atom of nitrogen

$\because$ $2\times 6\times 10^{23}$ atoms of N_2 has mass = 28*gm*

$\therefore$ 1 atom of N_2 has mass $=\frac{28}{2\times 6\times 10^{23}}$

$=2.3\times 10^{-23}gm$

(III) $1\times 10^{-10}g$ molecular weight of oxygen

g atomic weight

$=2\times 1\times 10^{-10}=2\times 10^{-10}g$

(IV) $1\times 10^{-10}g$ atomic weight of copper

So, order of increasing masses $\text{II} < \text{I} < \text{III} < \text{IV}$.

32. (d) $\frac{\text{wt. of metal hydroxide}}{\text{wt. of metal oxide}}=\frac{EM + EOH^-}{EM + EO^-}$

$=\frac{1.520}{0.995}=\frac{x+17}{x+8}=1.520x+1.520\times 8$

$=0.995x+0.995\times 17$

$1.520x+12.160=0.995x+16.915$

or $0.525x=4.755$

$x=\frac{4.755}{0.525}=9$.

33. (b) One ion carries $3\times 1.6\times 10^{-19}$ *coulomb*

Then 1 *gm* ion N^{3-} (1 mole) carries

$=3\times 1.6\times 10^{-19}\times 6.02\times 10^{23}$

$=2.89\times 10^{5}$ *coulomb*

34. (a) $\frac{C_P}{C_V}=1.4$ so, given gas is diatomic

11.2*L* $=3.01\times 10^{23}$ molecules

$\therefore$ No. of atoms $=3.01\times 10^{23}\times 2$

$=6.023\times 10^{23}$ *atoms*

36. (b) The acid is dibasic.

Molecular weight of $H_3PO_3=3+31+48=82$

$\therefore$ Equivalent weight

$=\frac{\text{Molecular weight}}{\text{Basicity}}=\frac{82}{2}$ = 41.

37. (b) $\because$ 22400 *ml* at NTP has 6.023×10^{23} molecule

$\therefore$ 1 *ml* at NTP has = $\frac{6.023\times 10^{23}}{22400}$

$= 0.0002688\times10^{23}$

$= 2.69\times10^{19}$.

38. (c) Sp. heat × atomic wt.= 6.4

0.16 × atomic wt.= 6.4

Atomic wt. $= \frac{6.4}{0.16} = 40$.

39. (a) Molecular weight of $C_{60}H_{122}$

$= 12\times60+122\times1$

$= 720+122 = 842$

$\because$ 6×10^{23} molecule $C_{60}H_{122}$ has mass = 842*gm*

$\therefore$ 1 molecule $C_{60}H_{122}$ has mass $\frac{842}{6\times10^{23}}$

$= 140.333\times10^{-23}\,gm = 1.4\times10^{-21}\,gm.$

40. (b) $C_2H_4 + 2O_2 \rightarrow 2CO_2 + 2H_2O$

$\because$ 28*gm* C_2H_4 requires 64*gm* oxygen

$\therefore$ 2.8×10^3 *gm* C_2H_4 requires =

$\frac{64}{28}\times2.8\times10^3\,gm = 6.4\times10^3\,gm$ = 6.4*kg*.

41. (c) 2.5 molal NH_4OH means 2.5 moles of NH_3 in 1000*g* H_2O (1000*cc* of solution)

Hence, 100*cc* solution of NH_3 requires = 0.25 mole

$= 0.25\times22.4L = 5.6L$.

42. (d) $d = \frac{M}{V}$; $1 = \frac{M}{V}$ or *M* = *V*; 18*gm* = 18*ml*

6×10^{23} molecule of water has volume =18*cc*

1 molecule of water has volume $= \frac{18}{6\times10^{23}}$

$= 3\times10^{-23}\,cm^3$.

43. (a) 100*gm* caffeine has 28.9*gm* nitrogen

194*gm* caffeine has = $\frac{28.9}{100}\times194 = 56.06gm$

$\therefore$ No. of atoms in caffeine $= \frac{56.06}{14} \approx 4$.

44. (d) Molecular weight of $(CHCOO)_2Fe = 170$

Fe present in 100*mg* of $(CHCOO)_2Fe$

$= \frac{56}{170}\times100mg = 32.9mg$

This is present in 400*mg* of capsule

% of *Fe* in capsule $= \frac{32.9}{400}\times100 = 8.2$.

45. (d) 1 atom has mass $= 10.86\times10^{-26}\,kg$

$= 10.86\times10^{-23}\,gm$

6.023×10^{23} atoms has mass =

$10.86\times10^{-23}\times6.023\times10^{23}$ = $65.40gm$

This is the atomic weight of *Zn*.

46. (b) $\because$ 1mole $(COOH)_2 . 2H_2O$ has 96*gm* oxygen

$\therefore$ 0.3 mole $(COOH)_2 . 2H_2O$ has

$96\times0.3 = 28.8gm$

$\therefore$ No. of gram atoms of oxygen $= \frac{28.8}{16} = 1.8$.

47. (c) Equimolecular proportion means both gases occupied equal volume $= \frac{2.24}{2} = 1.12L$

For CH_4:

22.4*L* CH_4 has mass $= 16gm$

1.12*L* CH_4 has mass $= \frac{16}{22.4}\times1.12 = 0.8gm$.

For C_2H_6

22.4*L* C_2H_6 has mass = 30*gm*

1.12*L* C_2H_6 has mass $= \frac{30}{22.4}\times1.12$

$= \frac{3.0}{2}gm = 1.5gm$

Total mass $= 1.5gm + 0.8gm = 2.3gm$.

48. (c) Let wt. of metal oxide = 100*gm*

wt. of metal = 53*gm*

wt. of oxygen = 47*gm*

Equivalent weight of oxygen

$= \frac{\text{wt.of metal}}{\text{wt.of oxygen}}\times8$

$= \frac{53}{47}\times8 = 9.02$

Valency

$= \frac{2\times V.D}{E+35.5} = \frac{2\times66}{9+35.5} = \frac{132}{44.5} = 2.96 \approx 3$

$\therefore$ Atomic weight

$=$ Equivalentweight × Valency

$= 9.02\times3 = 27.06$

49. (b) One gram of hydrogen combines with 80*gm* of bromine.

So, equivalent weight of bromine = 80*gm*

$\because$ 4*gm* of bromine combines with 1*gm* of *Ca*

$\therefore$ 80*gm* of bromine combines with =

$\frac{1}{4} \times 80 = 20$.

50. (b) $\overset{+2}{Mn}SO_4 \rightarrow \overset{+4}{Mn}O_2$

Change of valency $= 4 - 2 = 2$

$\therefore$ Equivalent weight $= \frac{M}{2}$.

51. (a)
$$\underset{\substack{2ml \\ 100ml}}{2PH_3} \rightarrow \underset{\text{(solid)}}{2P} + \underset{\substack{3ml \\ 150ml}}{3H_2}$$

Increase in volume $= 150ml - 100ml = 50ml$ increase.

52. (b) $Mg + 2HCl \rightarrow MgCl_2 + H_2$

$\because$ 24*g Mg* evolves 22.4*L* H_2 at STP

$\therefore$ 12*g Mg* evolves H_2 at STP $\frac{22.4}{24} \times 12$

=11.2*L* at STP.

53. (b) (a) 2*gm* atom of nitrogen = 28*gm*

(b) 6×10^{23} atoms of *C* has mass $= 12gm$

3×10^{23} atoms of *C* has mass

$= \frac{12 \times 3 \times 10^{23}}{6 \times 10^{23}} = 6gm$

(c) 1mole of *S* has mass = 32*gm*

(d) 7.0*gm* of *Ag*

So, lowest mass = 6*gm* of *C.*

54. (c) 1mole of any gas at STP occupies 22.4*L.*

55. (b) $\because$ 22400*cc* of gas at STP has 6×10^{23} molecules

$\therefore$ 1.12×10^{-7} of gas at STP has

$\frac{6 \times 10^{23} \times 1.12 \times 10^{-7}}{22400} = .03 \times 10^{14} = 3 \times 10^{12}$

.

56. (a) $\because$ 2.24*L* of gas has mass = 4.4*gm*

$\therefore$ 22.4*L* of gas has mass $= \frac{4.4}{2.24} \times 22.4 = 44$

So given gas is CO_2 because CO_2 has molecular mass=44.

57. (d) 1*L* of air =210*cc* O_2

22400*cc* = 1 mole

$210cc = \frac{1}{22400} \times 210 = 0.0093$.

58. (d) $\because$ 22.4*L* of a gas at STP has no. of molecules

$= 6.023 \times 10^{23}$

$\therefore$ 8.96*L* of a gas at STP has no. of molecules

$= \frac{6.02 \times 10^{23} \times 8.96}{22.4} = 2.408 \times 10^{23}$

$= 24.08 \times 10^{22}$.

59. (a) Given equivalent weight of metal = 9

Vapour density of metal chloride = 59.25

$\therefore$ molecular weight of metal chloride

$= 2 \times V.D = 2 \times 59.25 = 118.5$

$\therefore$ valency of metal

$= \frac{\text{molecular weight of metal chloride}}{\text{equivalnet weight of metal} + 35.5}$

Valency of metal $= \frac{118.5}{9 + 35.5} = \frac{118.5}{44.5} = 2.66$

Therefore atomic weight of the metal

=equivalent weight $\times$ valency

$= 9 \times 2.66 = 23.9$

60. (d) The density of gas $= \frac{\text{molecular wt. of metal}}{\text{volume}}$

$= \frac{45}{22.4} = 2\,gm\,litre^{-1}$

61. (c) Equivalent weight of bivalent metal = 37.2

$\therefore$ Atomic weight of metal $= 37.2 \times 2 = 74.4$

$\therefore$ Formula of chloride $= MCl_2$

Hence, molecular weight of chloride

$(MCl_2) = 74.4 + 2 \times 35.5 = 145.4$

62. (c) As we know that

Equivalent weight $= \frac{\text{weight of metal}}{\text{weight of oxygen}} \times 8$

$= \frac{32}{0.4} \times 8 = 64$

Vapour density $= \frac{\text{mol.wt}}{2}$

Mol. wt $= 2 \times V.D = 2 \times 32 = 64$

As we know that $n = \frac{\text{mol.wt}}{\text{eq.wt}} = \frac{64}{64} = 1$

Suppose, the formula of metal oxide be M_2O_n.

Hence the formula of metal oxide $= M_2O$.

63. (b) Molecular weight of NH_3 is 17

According to the mole concept

$17\,gm$ NH_3 has molecules $= 6.02 \times 10^{23}$

$\therefore$ $1\,gm\ NH_3$ has molecules $=\dfrac{6.02\times10^{23}}{17}$

$\therefore$ $4.25\,gm\ NH_3$ has molecules

$=\dfrac{6.02\times10^{23}\times4.25}{17}=1.5\times10^{23}\ molecule$

The mole concept

1. (a) $16g\ O_2$ has no. of moles $=\dfrac{16}{32}=\dfrac{1}{2}$

$14g\ N_2$ has no. of moles $=\dfrac{14}{28}=\dfrac{1}{2}$

No. of moles are same, so no. of molecules are same.

2. (b) $Na_2SO_4\ .10H_2O$

$=2\times23+32+4\times16+10\times18$

$=46+32+64+180=322gm$

$322gm\ Na_2SO_4.10H_2O$ contains = 224 gm oxygen

$32.2gm\ Na_2SO_4.10H_2O$ contains

$=\dfrac{32.2\times224}{322}=22.4\ gm$

3. (b) Molarity $=\dfrac{W(gm)\times1000}{\text{molecular wt.}\times V(ml.)}$

$=\dfrac{2.65\times1000}{106\times250}=0.1M$

10*ml* of this solution is diluted to 1000*ml*

$N_1V_1=N_2V_2$

$10\times0.1=1000\times x$

$x=\dfrac{0.1\times10}{1000}=0.001M$.

4. (c) According to definition of molar solution → A molar solution is one that contains one mole of a solute in one litre of the solution.

5. (a) $44g$ of CO_2 has $2\times6\times10^{23}$ atoms of oxygen

$4.4g$ of CO_2 has $=\dfrac{12\times10^{23}}{44}\times4.4$

$=1.2\times10^{23}$ atoms.

6. (b) $44g\ CO_2$ occupies 22.4*L* at STP

$4.4g\ CO_2$ occupies $=\dfrac{22.4}{44}\times4.4=2.24L$.

7. (a) Density $=\dfrac{\text{Mass}}{\text{Volume}}$; $1=\dfrac{g}{ml}$ or $g=ml$

$0.0018ml=0.0018gm$

No. of moles

$=\dfrac{\text{weight}}{\text{Molecular weight}}=\dfrac{0.0018}{18}=1\times10^{-4}$

$\therefore$ No. of water molecules =

$6.023\times10^{23}\times1\times10^{-4}$

$=6.023\times10^{19}$.

8. (c) $Ca_3P_2+6H_2O\rightarrow2PH_3+3Ca(OH)_2$

9. (d) Amount of gold $=19.7kg=19.7\times1000gm$ $=19700gm$

No. of moles $=\dfrac{19700}{197}=100$

$\therefore$ No. of atoms $=100\times6.023\times10^{23}$

$=6.023\times10^{25}$ atoms.

10. (c) $\because$ $100gm\ CaCO_3=6.023\times10^{23}$ molecules

$\therefore$ $10gm\ CaCO_3=\dfrac{6.023\times10^{23}}{100}\times10$

$=6.023\times10^{22}$ molecule

1 molecule of $CaCO_3$ = 50 protons

6.023×10^{22} molecule of $CaCO_3$

$=50\times6.023\times10^{22}$

$=3.0115\times10^{24}$

11. (b) $16gm$ of CH_4 = 1mole $=6.023\times10^{23}$ molecules.

12. (c) According to avogadro's hypothesis equal volumes of all gases under similar conditions of temperature and pressure contains equal no. of molecules.

14. (d) $d=\dfrac{M}{V}$ (d = density, M= mass, V =volume)

Since $d=1$

So, $M=V$

$18gm=18ml$

$18ml=N_A$ molecules (N_A = avogadro's no.)

$1000ml=\dfrac{N_A}{18}\times1000=55.555\ N_A$.

15. (a) This is fact.

16. (a) $\because$ 3 moles of oxygen is that in 1 mole of $BaCO_3$

∴ 1.5 moles of oxygen is that in mole of

$BaCO_3 = \frac{1}{3}\times 1.5 = \frac{1}{2} = 0.5$.

17. (b) The no. of molecules present in 1*ml* of gas at STP is known as Laschmidt number.

22400*ml* of gas has total no. of molecules

$= 6.023\times 10^{23}$

1*ml* of gas has total no. of molecules

$= \frac{6.023\times 10^{23}}{22400}$

$= 2.69\times 10^{19}$.

18. (b) ∵ 2*gm* of hydrogen $= 6.02\times 10^{23}$ molecules

∴ 1*gm* of hydrogen

$= \frac{6.02\times 10^{23}}{2} = 3.01\times 10^{23}$ molecule.

19. (a) Molecular weight of SO_2Cl_2

$= 32+32+2\times 35.5$ = 135*gm*

∵ 135 *gm* of SO_2Cl_2 = 1*gm* molecule

∴ 13.5*gm* of $SO_2Cl_2 = \frac{1}{135}\times 13.5 = 0.1$.

20. (a) (a) 34*gm* of water

∵ 18*gm* H_2O = 6.023×10^{23} molecule

∴ 34*gm* H_2O = $\frac{6.023\times 10^{23}}{18}\times 34$

$= 11.37\times 10^{23}$ mole

(b) 28*gm* of CO_2

∵ 44*gm* $CO_2 = 6\times 10^{23}$ molecules

∴ 28*gm* $CO_2 = \frac{6\times 10^{23}}{44}\times 28 = 3.8\times 10^{23}$

(c) 46*gm* of CH_3OH

∵ 32*gm* $CH_3OH = 6\times 10^{23}$ molecules

∴ 46*gm* $CH_3OH = \frac{6\times 10^{23}}{32}\times 46 = 8.625\times 10^{23}$

(d) ∵ 108*gm* of $N_2O_5 = 6\times 10^{23}$ molecules

∴ 54*gm* of $N_2O_5 = \frac{6\times 10^{23}}{108}\times 54 = 3\times 10^{23}$ molecules.

21. (b) Sodium oxide → Na_2O

Molecular weight = 46 +16 = 62

62*gm* of Na_2O = 1 mole

620*gm* of Na_2O = 10 mole.

22. (b) 2*gm* of oxygen contains atom $= \frac{2}{16} = \frac{1}{8}$ mole

also 4*g* of sulphur $= \frac{4}{32} = \frac{1}{8}$ mole.

23. (c) Molarity = mole/litre

∵ 1*cc* contains 1.17*gm*

∴ 1000*cc* contains 1170*gm* $\frac{1170gm}{\text{Mol.wt.}}$

$= \frac{1170}{36.5} = 32.05 mole/litre$ (Mol. wt. of *HCl*=36.5)

24. (a) 1 mole of sucrose contains 6.023×10^{23} molecules

∵ 1 molecule of sucrose has 45 atoms

∴ 6.023×10^{23} molecule of sucrose has $45\times 6.023\times 10^{23}$ atoms/mole

25. (a) wt of $CO_2 = 44$

mol wt of $CO_2 = 44$

No. of molecule

$= \frac{wt.of\ CO_2}{mol\,wt\ of\ CO_2}\times 6.02\times 10^{23}$

$= \frac{44}{44}\times 6.02\times 10^{23}$

$= 6.02\times 10^{23}$

26. (c) No. of atoms in one molecule

= no. of moles $\times 6.022\times 10^{23}$

$= 1.4\times 6.022\times 10^{23} = 8.432\times 10^{23}$

27. (d) As we know that four sodium atom are present in sodium ferrocyanide $[Na_4Fe(CN)_6]$

Hence, number of Na atoms = No. of moles × number of atom × Avogadro's number

$2\times 4\times 6.023\times 10^{23} = 48\times 10^{23}$

Percentage composition & Molecular formula

1. (a) ∵ 40*gm NaOH* contains 16*gm* of oxygen

∴ 100*gm* of *NaOH* contains $\frac{16}{40}\times 100$ =40*%* oxygen.

2. (a) Urea- $NH_2 - CO - NH_2$

∵ 60*gm* of urea contains 28*gm* of nitrogen

∴ 100*gm* of urea contains $\frac{28}{60}\times 100 = 46.66$.

3. (b) Based on facts.

4. (d) $C = 24gm,\ H = 4gm,\ O = 32gm$

So, Molecular formula $= C_2H_4O_2$

So, Empirical formula $= CH_2O$

(Simplest formula).

5. (a) $\because$ 0.0835 mole of compound contains 1*gm* of hydrogen

$\therefore$ 1*gm* mole of compound contain =

$\frac{1}{0.0835} = 11.97$

=12*gm* of hydrogen.

12 *gm* of H_2 is present in $C_2H_{12}O_6$

6. (b) Empirical formula of an acid is CH_2O_2

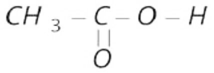
$(\text{Empiricalformula}) =$ Molecular formula

n = whole no. multiple *i.e.* 1,2,3,4.............

If $n = 1$ molecular formula CH_2O_2.

7. (b) Glucose - $C_6H_{12}O_6$

Ratio of *C*, *H* and *O* $= 1:2:1$

In acetic acid 

$CH_3 - \underset{\underset{O}{||}}{C} - O - H$

Ratio of *C*, *H* and *O* $1:2:1$.

Chemical stoichiometry

1. (c) $N = \frac{W(gm) \times 1000}{V \times \text{Eq.wt.}}$

1500*ml* of 0.1*N HCl* = 150*ml* (*N*)

$1 = \frac{W(gm) \times 1000}{150 \times 40}$, W (*gm*) $= \frac{150 \times 40}{1000} = 6gm$

.

2. (c) $N_1V_1 = N_2V_2;\ \frac{1}{2} \times 200 = \frac{1}{10} \times V_2;$

$V_2 = 1000ml$

Volume of water added $= 1000 - 200 = 800ml$.

3. (a) $2Ag_2CO_3 \xrightarrow{\Delta} 4Ag + 2CO_2 + O_2$

$2 \times 276\,gm \quad\quad 4 \times 108\,gm$

$\because$ $2 \times 276gm$ of Ag_2CO_3 gives $4 \times 108\,gm$

$\therefore$ $1\,gm$ of Ag_2CO_3 gives $= \frac{4 \times 108}{2 \times 276}$

$\therefore$ $2.76\,gm$ of Ag_2CO_3 gives

$\frac{4 \times 108 \times 2.76}{2 \times 276} = 2.16\,gm$

4. (c)

$$4NH_{3(g)} + 5O_{2(g)} \rightarrow 4NO_{(g)} + 6H_2O_{(g)}$$

$t = 0$	1	1	0	0
$t = t$	$1 - 4x$	$1 - 5x$	$4x$	$6x$

Oxygen is limiting reagent

So, $X = \frac{1}{5} = 0.2$ all oxygen consumed

Left $NH_3 = 1 - 4 \times 0.2 = 0.2$.

5. (c) $\because$ 100*gm Hb* contain = 0.33*gm Fe*

$\therefore$ 67200*gm Hb* = $\frac{67200 \times 0.33}{100}\,gm\,Fe$

gm atom of *Fe* = $\frac{672 \times 0.33}{56} = 4$.

6. (c) $\underset{132}{(NH_4)_2SO_4} \equiv 2NH_3 \equiv \underset{2(36.5)=73gm}{2HCl}$

$73g\,HCl \equiv 132g(NH_4)_2SO_4$

$292g\,HCl = 528g(NH_4)_2SO_4$

7. (c) $\underset{2(36+1+31+64)=264}{2(NH_4)_2HPO_4} \equiv \underset{62+80=142}{P_2O_5}$

% of $P_2O_5 = \frac{\text{wt.of } P_2O_5}{\text{wt of salt}} \times 100$

$= \frac{142}{264} \times 100 = 53.78\%$.

8. (b) $2Al + \frac{3}{2}O_2 \rightarrow Al_2O_3$

According to equation $\frac{3}{2}$ mole of O_2 combines with 2 mole *Al*.

2 mole *Al* = 54*gm*

9. (a) 0.5*gm Se* → 100*gm* peroxidase anhydrous enzyme

78.4*gm Se* $\rightarrow \frac{100 \times 78.4}{0.5} = 1.568 \times 10^4$

Minimum m.w. → molecule at least contain one selenium.

10. (d) $H_2O + \underset{27gm}{Al} + NaOH \rightarrow NaAlO_2 + \underset{\frac{3}{2} \times 22.4 = 33.6L}{\frac{3}{2}H_2}$

11. (c) In $Fe(CNS)_3 . 3H_2O$

% of $H_2O = \frac{3 \times 18}{284} \times 100 = 19\%$.

12. (d) $5S + 5O_2 \rightarrow 5SO_2;$ $\quad 5\,O_2 \equiv 5\,SO_2;$

$5 \times 64 = 320gm$.

13. (d) H_3PO_4 is tribasic so $N = 3M = 3 \times 1 = 3$.

14. (b) H_2SO_4 is dibasic $N = 2M = 2 \times 2 = 4$.

15. (a) For Dibasic acid $E = \frac{M}{2} = \frac{200}{2} = 100$

$$N = \frac{W \times 1000}{E \times V(\text{in } ml)}$$

$$\frac{1}{10} = \frac{W \times 1000}{100 \times 100} = W = 1gm.$$

16. (b)

$$N = \frac{10 \times \text{sp.gr.of thesolution} \times \text{wt.\% of sc}}{\text{Molecularwt.of solute} \times \text{Eq.}}$$

$$N = \frac{10 \times 1.71 \times 80 \times 98}{98 \times 49} = 27.9$$

18. (c) $2KMnO_4 + 3H_2SO_4 \rightarrow$

$K_2SO_4 + 2MnSO_4 + 3H_2O + [O]$

$2FeSO_4 + H_2SO_4 + [O] \rightarrow$
[Mohr-salt]

$Fe_2(SO_4)_3 + H_2O] \times 5$

$2KMnO_4 + 10FeSO_4 + 8H_2SO_4 \rightarrow$

$K_2SO_4 + 2MnSO_4 + 5Fe_2(SO_4)_3 + 8H_2O$

Mohr-salt reducing agent $KMnO_4 / H^+ \rightarrow$ oxidising agent

19. (d) Atomic weight = Equivalent weight × Valency

$= 8.9 \times 3 = 26.7$

$\left(\text{Valency} = \frac{26.89}{8.9} \approx 3\right)$.

20. (c) $MW = 2 \times V.D. = 2 \times 22 = 44$.

21. (d)

$$\underset{+7}{2KMnO_4} + \underbrace{3H_2SO_4 \rightarrow K_2SO_4 + 2MnSO_4}_{\text{Change by 5}} \underset{+2}{} + 3H_2O + 5[O$$

$$\text{Eq. wt.} = \frac{\text{Mol.wt.}}{5}$$

22. (c) Dibasic acid *NaOH;* $N_1V_1 = N_2V_2$

$\frac{W}{E} \times 1000 = \frac{1}{10} \times 25$; $\frac{0.16}{E} \times 1000 = \frac{25}{10}$

$M = 2 \times E = 2 \times 64 = 128$.

23. (d) *NaOH* *HCl*

$N_1V_1 = N_2V_2$; $20 \times \frac{1}{10} = \frac{1}{20} \times V$; V = 40*ml.*

24. (a) $NV = N_1V_1 + N_2V_2$

$0.2 \times 2 = 0.5x + 0.1(2 - x)$

$0.4 = 0.5x + 0.2 - 0.1x$

$0.2 = 0.4x$

$x = \frac{1}{2}L = 0.5L$

25. (d) $NV = N_1V_1 + N_2V_2 + N_3V_3$

$N \times 1000 = 1 \times 5 + \frac{1}{2} \times 20 + \frac{1}{3} \times 30$

$= 5 + 10 + 10 = 25$

$N = 0.025 = \frac{N}{40}$.

26. (b)

$$\begin{array}{llll} & NH_{3(g)} + & HCl_{(g)} \rightarrow & NH_4Cl_{(s)} \\ t = 0 & 20ml & 40ml & 0 \\ t = t & 0 & 20ml & \text{solid} \end{array}$$

Final volume = 20*ml*.

27. (b) $KMnO_4$ Oxalic acid

$\frac{M_1V_1}{n_1} = \frac{M_2V_2}{n_2}$; $\frac{20 \times 0.1}{2} = \frac{M_2V_2}{5}$;

$M_2V_2 = 5$.

28. (b) Acidic medium $E = \frac{M}{5} = \frac{158}{5} = 31.6gm$.

29. (c) 0.1 *M* $AgNO_3$ will react with 0.1 *M NaCl* to form 0.1 *M* $NaNO_3$. But as the volume is doubled, conc. of $NO_3^- = \frac{0.1}{2} = 0.05M$

30. (a) Acid base

$N_1V_1 = N_2V_2$; $N_1 \times 30 = 0.2 \times 15$;

$N_1 = 0.1N$

31. (b) (I) Phenopthalein indicate partial neutralisation of $Na_2CO_3 \rightarrow NaHCO_3$

Meq. of Na_2CO_3 + Meq. of *NaOH* = Meq. of *HCl*

$\frac{W}{E} \times 1000 + \frac{W}{E} \times 1000 = NV$

(Suppose $Na_2CO_3 = agm$, *NaOH = b gm*)

$\frac{a}{106} \times 1000 + \frac{b}{40} \times 1000 = 300 \times 0.1$ .....(1)

(II) Methyl orange indicate complete neutralisation

HCl *HCl*

$N_1V_1 = N_2V_2$, $25 \times 0.2 = 0.1 \times$

V_2 so$V_2 = 50ml$ excess

$\therefore \frac{a}{53} \times 1000 + \frac{b}{40} \times 1000 = 350 \times 0.1$ .....(2)

From (1) and (2) $b = 1gm$.

32. (c) From solution of (31)

From equation (1)

$a = Na_2CO_3 = 0.53gm$.

33. (b) $(H_2SO_4)\frac{M_1V_1}{n_1} = \frac{M_2V_2}{n_2}(NaOH)$

$\frac{1 \times V_1}{1} = \frac{1 \times 10}{2}$; $V_1 = 5ml$.

34. (c) Atom in highest oxidation state can oxidize iodide to liberate I_2 which is volumetrically measured by iodometric titration using hypo.

$2I^- \to I_2$

$Pb^{+2} \to$ Lowest oxidation state can not oxidise iodide to I_2.

35. (d) $KMnO_4 =$ Mohr salt

$\frac{M_1V_1}{n_1} = \frac{M_2V_2}{n_2}$; $\frac{0.1 \times 10}{1} = \frac{M_2V_2}{5}$;

$M_2V_2 = 5$.

36. (d) The equivalent weight of $H_3PO_4 = \frac{\text{molecular weight}}{2}$

$\because$ mole wt of H_3PO_4 = 3 + 31 + 64 = 98

$\therefore \frac{98}{2} = 49$

37. (b) $Ba(OH)_2 + CO_2 \to BaCO_3 + H_2O$

Atomic wt. of $BaCO_3 = 137 + 12 + 16 \times 3$ = 197

No. of mole $= \frac{\text{wt. of substance}}{\text{mol wt.}}$

$\because$ 1 mole of $Ba(OH)_2$ gives 1 mole of $BaCO_3$

$\therefore$ 205 mole of $Ba(OH)_2$ will give .205 mole of $BaCO_3$

$\therefore$ wt. of 0.205 mole of $BaCO_3$ will be

$.205 \times 197 = 40.385gm \approx 40.5\,gm$

38. (d) $N_1 = 0.5N \to 10mg$ per mL

$N_2 = \frac{10 \times 10^{-3}\,gm}{40 \times 1} \times 1000$ =0.25N

$V_1 = 500ml$, $V_2 = ?$

$N_1V_1 = N_2V_2$; $0.5 \times 500 = 0.25 \times V_2$

$V_2 = 1000mL$ final volume water added = 1000 – 500

= 500mL.

39. (a) eq. of $KMnO_4$ = eq. of $Fe(C_2O_4)$

$x \times 5 = 1 \times 3$

$x = 0.6$

40. (b)

Element	At.wt.	Mole	Ratio	Empirical formula
C =86%	12	7.1	1	CH_2
H =14%	1	14	2	Beleongs to alkene C_nH_{2n}

41. (b) $AgNO_3 \equiv 2Ag^+ + \underset{(H_2S)}{S^{2-}} \to Ag_2S$

$\because$ 2 mole → 1 mole [100×1 =100 millimole]

$\therefore$ 100 miliimole →50 millimole H_2S required

$CuSO_4 \equiv Cu^{+2} + \underset{(H_2S)}{S^{2-}} \to CuS$

$\because$ 1 mole →1 mole [100×1=100 millimole]

$\therefore$ 100 millimole → 100 millimole H_2S required

Ratio $\frac{50}{100} = \frac{1}{2}$.

42. (c) At room temperature

$2H_{2(g)} + O_{2(g)} \to 2H_2O_{(l)}$

t =0 50ml 50ml 0

t =t 50 – 2x 50 – x 2x

=0 25$gases$ (50)liquid

In this case H_2 is limiting reagent

x = 25ml

At 110°C $2H_{2(g)} + O_{2(g)} \to 2H_2O_{(g)}$

$V_{gas} = 75ml$

t =t 0 25ml 50ml

43. (c) $\overset{+2}{Cu}SO_4 + 2KI \to K_2SO_4 + \overset{+2}{Cu}I_2$;

$2\overset{+2}{Cu}I_2 \to \overset{+1}{Cu}I_2 + I_2$

$I_2 + 2Na_2S_2O_3 \to 2NaI + Na_2S_4O_6$

Eq. wt. Of $CuSO_4.5H_2O$ = Mol.wt. = 250

100 ml of 0.1 N hypo ≡ 100 ml of 0.1 N $CuSO_4.5H_2O$

$= \frac{250 \times 0.1 \times 100}{100} = 2.5\,gm$

44. (d) $HNO_3 + KOH \to KNO_3 + H_2O$

$\frac{12.6}{63}$ = 0.2 mole; $HNO_3 \equiv KOH$

0.2 mole ≡ 0.2 mole

$0.2 \times 56 = 11.2 gm$.

45. (a) Isobutane and *n*-butane $[C_4H_{10}]$ have same molecular formula;

$C_4H_{10} + \frac{13}{2} O_2 \rightarrow 4CO_2 + 5H_2O$

For 58*gm* of C_4H_{10} 208 *gm* O_2 is required then

for 5 *kg* of C_4H_{10} $O_2 = \frac{5 \times 208}{58} = 17.9 kg$

46. (b) $n = \frac{16.8}{22.4} = 0.75$ mole of H_2 and O_2

$\underset{2:1}{2H_2O \rightarrow 2H_2 + O_2} \quad 0.75 < \begin{matrix} 0.25 & O_2 \\ 0.25 & H_2 \end{matrix}$

2 mole H_2 – 2 mole H_2O

0.5 mole H_2 – 0.5 mole H_2O = 9*gm*.

47. (a) ∵ 3*ml* (*O*) → 1*ml* O_3

30*ml* (*O*) → 10*ml* O_3

$x = \frac{150 \times 10}{100} = 15ml$

V of O_2 + *V* of $O_3 = 135 + 10 = 145ml$

Turpentine oil absorb ozone.

48. (a) 50% *HCl* itself means 50*gm HCl* react with 100*gm* sample

% Purity $= \frac{50}{100} \times 100 = 50\%$.

49. (a) $AgNO_3 + HCl \rightarrow AgCl + HNO_3$

$\frac{30}{170} \quad \frac{500 \times 0.2}{1000}$

t =0 0.176 mole 0.1 mole limiting =14.345*gm*

t =*t* 0.076 mole 0 0.1mole

50. (d) $KMnO_4 \quad FeSO_4$

$\frac{M_1V_1}{n_1} = \frac{M_2V_2}{n_2}$; $M_1V_1 = \frac{n_1}{n_2} M_2V_2$

$= \frac{2}{10} \times 10 \times \frac{1}{10} = \frac{1}{5} = 0.2$

For (d), $M_1V_1 = 0.02 \times 10 = \frac{1}{5}$

51. (c) $\underset{1 \text{ mol.}}{ROH} + CH_3MgI \rightarrow \underset{1 \text{ mol}=22400cc}{CH_4 + Mg\begin{matrix} OR \\ I \end{matrix}}$

1.12 *mL* is obtained from 4.12 *mg*

∴ 22400 *mL* will be obtained from

$\frac{4.12}{1.12} \times 22400 mg = 84.2 g$

52. **(b)**

Element	%(a)	At.wt. (b)	a/b	Ratio
X	50	10	5	2
Y	50	20	2.5	1

Simplest formula $= X_2Y$

53. (a) $A_3(BC_4)_2 = 3 \times 2 + [5 + (-2 \times 4)]_2 = 0$.

54. (b) $\underset{10gm}{CaCO_3} \rightarrow CaO + CO_2$

90% pure 9*gm* $= \frac{9}{100}$ mole

$CaCO_3 \equiv CO_2 = 0.09$ mole

At NTP Vol. $CO_2 = 0.09 \times 22.4 = 2.016L$.

55. (b) $Cd^{+2} + S^{2-} \rightarrow CdS$

20×1= 20

$Cu^{+2} + S^{2-} \rightarrow CuS$

20×0.5 =10

Ratio = $2:1$

56. (b) $Mg^{+2} \equiv H_2$

$n = \frac{12gm}{24gm} = \frac{1}{2}$ mole of H_2

57. (a) $\underset{1\text{mole}}{Mg} + \underset{0.5\text{mole}}{\frac{1}{2} O_2} \rightarrow MgO$

0.5 mole of oxygen react with 1 mole of *Mg*

1.5 mole of oxygen react with $\frac{1.5}{0.5} = 3$ mole

$24 \times 3 = 72gm$.

58. (c) $\underset{100g}{CaCO_3} + \underset{2N}{2HCl} \rightarrow CaCl_2 + \underset{44\,g}{CO_2} + H_2O$

100 *g* $CaCO_3$ with 2 *N HCl* gives 44 *g* CO_2

100 *g* $CaCO_3$ with 1 *N HCl* gives 22 *g* CO_2

Critical Thinking Questions

2. (b) H_2O contains *H* and *O* in a fixed ratio by mass. It illustrates the law of constant composition.

3. (b) 100 *g* of $ZnSO_4$ crystals are obtained from =22.65*g Zn*

1g of $ZnSO_4$ crystals will be obtained from $= \frac{22.65}{100} g\ Zn$

20 g of $ZnSO_4$ crystals obtained from

$= \frac{22.65}{100} \times 20 = 4.53\ g$

4. (a) If same volume is occupied by the gas, the no. of molecules are same, so no. of moles are same.

1 mole of N_2 gas $= 2 \times 14 = 28gm$

1 mole of CO gas $= 12 + 16 = 28gm$

5. (c) Heat capacity of water per gram $= \frac{75}{18} = 4.17$

$Q = mST$

$1000 = 100 \times 4.17 \times t$

$t = \frac{1000}{100 \times 4.17} = 2.4\ K$.

6. (b) $\because$ 8gm sulphur is present in 100gm of substance

$\therefore$ 32gm sulphur will present $= \frac{100}{8} \times 32 = 400$.

7. (b) (a) 6.023×10^{23} molecules of CO_2

No. of atoms $= 3 \times 6.023 \times 10^{21} =$

18.069×10^{21} atoms

(b) 22.4L of CO_2

No. of atoms = $6.023 \times 10^{23} \times 3$

$= 18.069 \times 10^{23}$ atoms

(c) 0.44gm of CO_2

No. of moles $= \frac{0.44}{44} = \frac{1}{100} \times 6.023 \times 10^{23}$ moles

$= 6.023 \times 10^{21}$ moles $= 3 \times 6.023 \times 10^{21}$ atoms

18.069×10^{21} atoms

8. (b) It is about 22.4L.

9. (a) 200mg of CO_2 = $200 \times 10^{-3} = 0.2gm$

44gm of CO_2 = 6×10^{23} molecules

0.2gm of CO_2 = $\frac{6 \times 10^{23}}{44} \times 0.2 = 0.0272 \times 10^{23}$

$= 2.72 \times 10^{21}$ molecule

Now 10^{21} molecule are removed.

So remaining molecules $= 2.72 \times 10^{21} - 10^{21}$

$= 10^{21}(2.72 - 1) = 1.72 \times 10^{21}$ molecules

Now, 6.023×10^{23} molecules = 1mole

1.72×10^{21} molecules

$= \frac{1 \times 1.72 \times 10^{21}}{6.023 \times 10^{23}} = 0.285 \times 10^{-2}$

$= 2.85 \times 10^{-3}$.

10. (d)

$$2K_2Cr_2O_4 + 2HCl \rightarrow K_2Cr_2O_7 + 2KCl + H_2O$$

11. (a) Meq of Mg^{+2} $\equiv$ Meq of washing soda

$\frac{W}{E} \times 1000 = Mg^{+2}$; $EW = \frac{24}{2} = 12$

$\frac{12 \times 10^{-3}}{12} \times 1000 = 1$.

12. (c) $K_2Cr_2O_7 + 4H_2SO_4 \rightarrow K_2SO_4 + Cr_2(SO_4)_3 + 4H_2O + 3[O]$

+12/twoatom +6/twoatom

Change by 6

$$\text{Eq. wt.} = \frac{\text{Mol.wt.}}{6}$$

13. (a) $KMnO_4$ = Mohr salt

$\frac{M_1V_1}{1} = \frac{M_2V_2}{5} = \left[\frac{W}{M \times V} \times 1000\right] \times \frac{V_2}{5}$

$\left[\frac{W \times 1000}{58 \times 1000}\right] \times 18 = \frac{3.92 \times 1000}{392 \times 1000} \times \frac{20}{5}$

W=3.476gm/L.

14. (d) Volume m of HCl neutralised by $NaOH$ = (Caustic soda) = V_1

$N_1V_1 = N_2V_2$; $0.1 \times V_1 = 0.2 \times 30$;

$V_1 = 60ml$

V total (HCl) = 100ml

V_1 = 60ml

40ml

40ml 0.1N HCl is now neutralised by KOH (0.25N) →

(HCl) $N_1V_1 = N_2V_2$ (KOH)

$0.1 \times 40 = 0.25 \times V_2$; $V_2 = 16ml$.

15. (c) $BCl_3 + 3[H] \rightarrow B + 3HCl$

$BCl_3 + \frac{3}{2}H_2 \rightarrow B + 3HCl$; $B = \frac{21.6}{10.8} = 2$ mole

$B \equiv \frac{3}{2} H_2$

1mole $\equiv \frac{3}{2}$ mole ; 2 mole – 3 mole

$V = 3 \times 22.4 = 67.2L$.

16. (c) $n = \frac{W}{M} = \frac{V}{22400}$; $\frac{W}{16} = \frac{112}{22400}$; $W = 0.08gm$.

17. (a) $\%C = \frac{12}{44} \times \frac{W_{CO_2}}{W} \times 100$

$= \frac{12}{44} \times \frac{2.63}{0.858} \times 100 = 83.6\%$

$\%H = \frac{2}{18} \times \frac{W_{H_2O}}{W} \times 100$

$= \frac{2}{18} \times \frac{1.28}{.858} \times 100 = 16.4\%$

Element	%(a)	At.wt. (b)	a/b	Ratio	× 3 7
C	83.6	12	6.96	1	
H	16.4	1	16.4	2.3	

$C_3H_7 = 12 \times 3 + 7 = 43gm$.

18. (b) $\underset{+4}{SO_2} + 2H_2O \rightarrow \underset{0}{S} + 2H_2O_2$

$EW = \frac{M}{4} = \frac{64}{4} = 16$; Twice $16 \times 2 = 32$

Assertion & Reason

1. (e) We know that from the reaction $H_2 + Cl_2 \rightarrow 2HCl$ that the ratio of the volume of gaseous reactants and products is in agreement with their molar ratio. The ratio of $H_2 : Cl_2 : HCl$ volumes is $1:1:2$ which is the same as their molar ratio. Thus volume of gas is directly related to the number of moles. Therefore, the assertion is false but reason is true.

2. (e) We know that molecular weight of substance is calculated by adding the atomic weight of atoms present in one molecules. We also know that molecular weight of oxygen (O_2) =2*x* (Atomic weight of oxygen) $= 2 \times 16 = 32\ a.m.u.$ Atomic weight of oxygen is 16, because it is 16 times heavier than1/12th of carbon atom. Therefore assertion is false but reason is true.

3. (c) According to Dalton's atomic theory atoms can neither be created nor destroyed and according to berzelius hypothesis, under similar condition of temperature and pressure equal volumes of all gases contain equal no. of atom. Therefore assertion is true but reason is false.

4. (e) One mole of any substance corresponding to 6.023×10^{23} entities is respective of its weight.

Molecular weight of $SO_2 = 32 + 2 \times 16 = 64gm$.

Molecular weight of $O_2 = 16 \times 2 = 32gm$.

$\therefore$ Molecular weight of SO_2 is double to that of O_2.

5. (d) 1.231 has four significant figures all no. from left to right are counted, starting with the first digit that is not zero for calculating the no. of significant figure.

6. (d) Molar volume (at NTP) = 22.4*L*

Now 22.4*L* of $N_2 =$ volume occupied by one mole of $N_2 = 28gm = 6.023 \times 10^{23}$ molecules.

Similarly, $O_2 = 2 \times 16 = 32gm$,

$32gm = 6.023 \times 10^{23}$ molecules = 22.4*L*

$\therefore$ $22.4L = 6.023 \times 10^{23}$ or

$5.6L = \frac{6.023 \times 10^{23} \times 5.6}{22.4}$

$= \frac{1}{4} \times 6.023 \times 10^{23}$

According to avagadro's hypothesis equal volume of all gases contain equal no. of molecules under similar condition of temperature and pressure.

7. (a) For universally accepted atomic mass unit in 1961, *C*-12 was selected as standard. However the new symbol used is '*v*' (unified mass) in place of *amu.*

8. (c) Vapour density of $B = \frac{M}{2}$, Vapour density of $A = 4 \times \frac{M}{4} = 2M$

Molecular mass of $A = 2 \times 2M = 4M$.

9. (a) Pure water always contains hydrogen and oxygen in the ratio $1:8$ by mass. This is in accordance with the law of constant composition.

10. (b) The number of moles of a solute present in litre of solution is known is as molarity (*M*).

The total no. of molecules of reactants present in a balanced chemical equation is known as molecularity. For example,

$PCl_5 \rightarrow PCl_3 + Cl_2$ (Unimolecular)

$2HCl \rightarrow H_2 + I_2$ (Bimolecular)

$\therefore$ Molarity and molecularity are used in different sense.

11. (a) Both assertion and reason are true and reason is the correct explanation of assertion.

12. (e) Equivalent wt. of *Cu* in *CuO* = $\frac{63.6}{2} = \frac{\text{At.wt.}}{\text{Valency}}$

=31.8

Equivalent wt. of *Cu* in $Cu_2O = \frac{63.6}{1}$ =63.6

(Valency of *Cu* =1).

13. (e) Mass spectrometer is the instrument used for the determination of accurate atomic mass and the relative abundance of the isotopes.

14. (a) Both assertion and reason are true and reason is the correct explanation of assertion.

15. (a) Example of isomorphous compounds are K_2SO_3, K_2CrO_4, K_2SeO_4 (valency of *S*, *Cr*, *Se* = 6) and $ZnSO_4\ .\ 7H_2O$, $MgSO_4\ .\ 7H_2O$, $FeSO_4\ .\ 7$

(valency of *Zn*, *Mg*, *Fe* =2).

16. (b) No. of atoms present in a molecules of a gaseous element is called atomicity.

For example, O_2 has two atoms and hence its atomicity is 2.

17. (a) 12*gm* of *C*-12 contain 6.023×10^{23} atom

$\therefore \quad \frac{12}{6.023} \times 10^{-23} = 1.66 \times 10^{-24}$.

Chemical Arithmetic

SET Self Evaluation Test - 1

1. A mixture of sand and iodine can be separated by **[Kerala CEE 2002]**

(a) Crystallisation (b) Sublimation

(c) Distillation (d) Fractional distillation

2. The element similar to carbon is

(a) Mg (b) Mn

(c) Sn (d) Po

2. The law of multiple proportions was proposed by **[IIT 1992]**

(a) Lavoisier (b) Dalton

(c) Proust (d) Gay-Lussac

4. 1 *L* of N_2 combines with 3 *L* of H_2 to form 2*L* of NH_3 under the same conditions. This illustrates the

(a) Law of constant composition

(b) Law of multiple proportions

(c) Law of reciprocal proportions

(d) Gay-Lussac's law of gaseous volumes

5. One sample of atmospheric air is found to have 0.03% of carbon dioxide and another sample 0.04%. This is evidence that

(a) The law of constant composition is not always true

(b) The law of multiple proportions is true

(c) Air is a compound

(d) Air is a mixture

6. One part of an element *A* combines with two parts of another *B*. Six parts of the element *C* combine with four parts of the element *B*. if *A* and *C* combine together the ratio of their weights will be governed by **[AMU 1984]**

(a) Law of definite proportion

(b) Law of multiple proportion

(c) Law of reciprocal proportion

(d) Law of conservation of mass

7. The maximum amount of $BaSO_4$ precipitated on mixing equal volumes of $BaCl_2$ (0.5 *M*) with H_2SO_4 (1*M*) will correspond to **[AIIMS 1997]**

(a) 0.5 *M* (b) 1.0 *M*

(c) 1.5 *M* (d) 2.0 *M*

8. Crystals of which pair are isomorphous **[MP PMT 1985]**

(a) $ZnSO_4, SnSO_4$ (b) $MgSO_4, CaSO_4$

(c) $ZnSO_4, MgSO_4$ (d) $PbSO_4, NiSO_4$

9. M is the molecular weight of $KMnO_4$. The equivalent weight of $KMnO_4$ when it is converted into K_2MnO_4 is

(a) *M* (b) $M/3$

(c) $M/5$ (d) $M/7$

10. An aqueous solution of 6.3 *g* of oxalic acid dihydrate is made up of to 250 *ml*. The volume of 0.1 $N\ NaOH$ required to completely neutralise 10 *ml* of this solution is **[IIT 2001]**

(a) 40 *ml* (b) 20 *ml*

(c) 10 *ml* (d) 4 *ml*

11. The normality of orthophosphoric acid having purity of 70% by weight and specific gravity 1.54 would be **[CPMT 1992]**

(a) 11*N* (b) 22*N*

(c) 33*N* (d) 44*N*

12. The equivalent weight of phosphoric acid (H_3PO_4) in the reaction, $NaOH + H_3PO_4 \rightarrow NaH_2PO_4 + H_2O$ is **[AIIMS 1999; BHU 2005]**

(a) 25 (b) 49

(c) 59 (d) 98

13. Volume of 0.6 *M NaOH* required to neutralize $30\,cm^3$ of 0.4 *M HCl* is **[KCET 1995]**

(a) $30\,cm^3$ (b) $20\,cm^3$

(c) $50\,cm^3$ (d) $45\,cm^3$

14. One mole of potassium dichromate completely oxidises the following number of moles of ferrous sulphate in acidic medium **[MP PET 1998]**

(a) 1 (b) 3

(c) 5 (d) 6

15. The number of equivalents of $Na_2S_2O_3$ required for the volumetric estimation of one equivalent of Cu^{2+} is

[Kerala MEE 2000]

(a) 1 (b) 2

(c) 3/2 (d) 3

Answers and Solutions

(SET -1)

1. (b) Iodine shows sublimation and hence volatalizes on heating, the vapour condenses on cooling to give pure iodine.

2. (c) Carbon and tin both are same group elements so have similarities in properties.

3. (b) Law of multiple proportions was proposed by Dalton and verified by Berzelius.

4. (d) Gay- Lussac's law : The volumes of the reacting gases and those of the gaseous products bear the simple ratio (also called the law of gaseous volumes).

5. (d)

6. (c) The weights of two elements combining with a fixed amount of the third element will bear the same ratio(or simple multiple of it) in which they themselves react.

7. (a) $BaCl_2 + H_2SO_4 \to BaSO_4 + 2HCl$

One mole of $BaCl_2$ reacts with one mole of H_2SO_4. Hence 0.5 mole will react with 0.5 mole of H_2SO_4 *i.e.* $BaCl_2$ is the limiting reagent.

8. (c) Isomorphous substance molecules contain the same number of atoms bonded in similar fashion.

9. (a) $K\overset{+7}{Mn}O_4 \to K_2\overset{+6}{Mn}O_4$

Change in 0.5 per atom $= 7 - 6 = 1$

$\therefore$ Equivalent weight of $KMnO_4$

$$= \frac{\text{Molecular weight of } KMnO_4}{\text{Change of 0.5 per atom}} = \frac{M}{1} = M.$$

10. (a) Oxalic acid $NaOH$

$N_1V_1 = N_2V_2$

$$\left[\frac{W}{E}\times\frac{1000}{V}\right]\times V_1 = N_2V_2$$

$\frac{6.3}{63}\times\frac{1000}{250}\times 10 = 0.1\times V$ V= 40*ml.*

11. (a) 70% by weight $70gm\,H_3PO_4 \to 100gm$ solution/sample

$V = \frac{W}{d} = \frac{100}{1.54}$ $N = \frac{70\times 1000}{98\times 100/1.54} = 11N$.

12. (d) $\underset{(PO_4^{-3})}{NaOH + H_3PO_4} \to \underset{(NaPO_4^{-2})}{NaH_2PO_4}$

$$EW = \frac{MW}{\text{no. of ionisable } H^+} = \frac{98}{1}.$$

13. (b) $NaOH$ HCl

$N_1V_1 = N_2V_2$; $0.6\times V_1 = 0.4\times 30$;

$V_1 = 20ml$.

14. (d) $\underset{n=6}{Cr_2O_7^{--} \to Cr^{3+}}$; $\underset{n=1}{Fe^{++} \to Fe^{+++}}$

eq. of $K_2Cr_2O_7$ = eq. of $FeSO_4$

$1\times 6 = x\times 1$

15. (b) $Cu^{2+} + 2I^- \to CuI_2$ $2CuI_2 \to Cu_2I_2 + I_2$

$I_2 + 2Na2S_2O_3 \to 2NaI + Na_2S_4O_6$

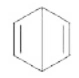
$Cu^{2+} \equiv 2Na_2S_2O_3$

***

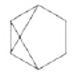
Aromatic Substitution Notes + Practice Questions

The Structure of Benzene

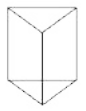
There are many possibilities, among them four are shown in figure below.



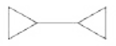
"Dewar" benzene
bicyclo[2.2.0]hexa-2,5-diene



benzvalene



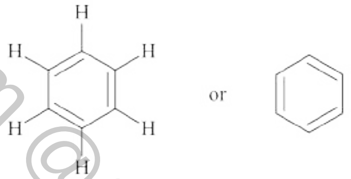
"Ledenberg" benzene



3,3'-Bicyclopropenyl

But above structures are not able to explain the properties of benzene.

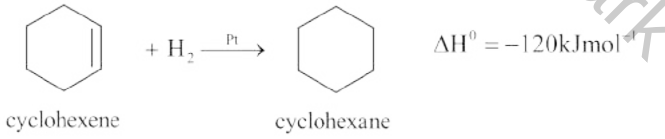
A Resonance Picture of Benzene: In1865, August Kekulé, the originator of the structural theory proposed the first definite structure for benzene, a structure that is still used today (although as we shall soon see, we give it a meaning different from the meaning Kekulé gave it). Kekulé suggested that the carbon atoms of benzene are in a ring, that they are bonded to each other by alternating single and double bonds, and that one hydrogen atom is attached to each carbon atom. This structure satisfied the requirements of the structural theory that carbon atoms form four bonds and that all the hydrogen atoms of benzene are equivalent.



The Kekulé formula for benzene

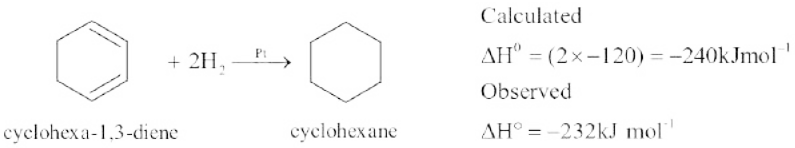
The Stability of Benzene: We have seen that benzene shows unusual behaviour by undergoing substitution reactions when, on the basis of its Kekulé structure, we should expect it to undergo addition. Benzene is unusual in another sense. It is more stable than the Kekulé structure suggests. To see how, consider the following thermochemical results.

Cyclohexene, a six-membered ring containing one double bond, can be hydrogenated easily to cyclohexane. When the ΔH^0 for this reaction is measured it is found to be -120kJ mol^{-1}, very much like that of any similarly substituted alkene.

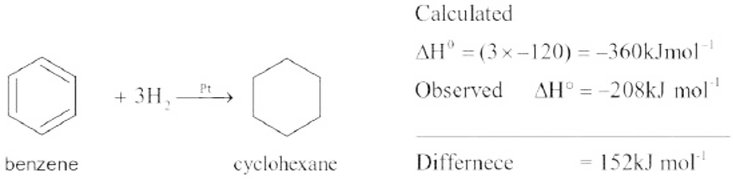


We would expect that hydrogenation of 1,3-cyclohexadiene would liberate roughly twice as much heat and thus have a $\Delta H°$ equal to about -240 kJ mol^{-1}. When this experiment is done, the result is $\Delta H° = -232$ kJ mol^{-1}. This result is quite close to what we calculated, and the difference can be explained by taking into account the fact that compounds containing conjugated double bonds are usually somewhat more stable than those that contain isolated double bonds.

In addition reaction with H_2/Pt 1, 3 diene is definitely more reactive than monoene because of more unsaturation. But between two different dienes, conjugated and isolated, conjugate is more stable because of higher stabilisation.

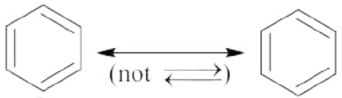


If we extend this kind of thinking, and if benzene is simply 1,3,5-cyclohexatriene, we would predict benzene to liberate approximately –360 kJ mol^{-1} (3 × –120) when it is hydrogenated. When the experiment is actually done the result is surprisingly different. The reaction is exothermic, but only by –208 kJ mol^{-1}.



When these results are represented as in figure, it becomes clear that benzene is much more stable than we calculated it to be. Indeed, it is more stable than the hypothetical 1,3,5-cyclohexatriene by 152 kJ mol^{-1}. This difference between the amount of heat actually released and that calculated on the basis of the Kekulé structure is now called the resonance energy of the compound.

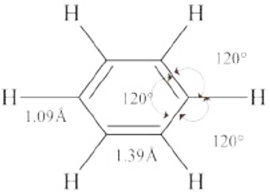
The Resonance Explanation of the Structure of Benzene: A basic postulate of resonance theory is that whenever two or more Lewis structures can be written for a molecule that differ only in the positions of their electrons, none of the structures will be in complete accord with the compound’s chemical and physical properties. If we recognize this, we can now understand the true nature of the two Kekulé structures (I and II) for benzene. The two Kekulé structures differ only in the positions of their electrons. Structure I and II, then, do not represent two separate molecules in equilibrium as Kekulé had proposed. Instead, they are the closest we can get to a structure for benzene within the limitations of its molecular formula, the classic rules of valence, and the fact that the six hydrogen atoms are chemically equivalent. The problem with the Kekulé structures is that they are Lewis structures, and Lewis structures portray electrons in localized distributions. (With benzene, as we shall see, the electrons are delocalized). Resonance theory, fortunately, does not stop with telling us when to expect this kind of trouble; it also gives us a way out. Resonance theory tells us to use structures I and II as resonance contributors to a picture of the real molecules of benzene. As such, I and II should be connected with a double headed arrow and not with two separate ones (because we must reserve the symbol of two separate arrows for chemical equilibria). Resonance contributors, we emphasize again, are not in equilibrium. They are not structures of real molecules. They are the closest we can get if we find found by simple rules of valence, but they are very useful in helping us to visualize the actual molecule as a hybrid.



I

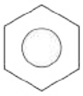
II

Look at the structures carefully. All of the single bonds in structure I are double bonds in structure II. If we blend I and II, that is, if we fashion a hybrid of them, then the carbon-carbon bonds in benzene are neither single bonds nor double bonds. Rather, they have a bond order between that of a single bond and that of a double bond. Bond order of benzene ring is found to be 1.5. This is exactly what we find experimentally. Spectroscopic measurements show that the molecule of benzene is planar and that of all of its carbon-carbon bonds are of equal length. Moreover, the carbon-carbon bond lengths in benzene figure are 1.39Å, a value in between that for a carbon-carbon single bond between sp^2 hybridized atoms (1.47Å) and that for a carbon-carbon double bonds (1.33Å)



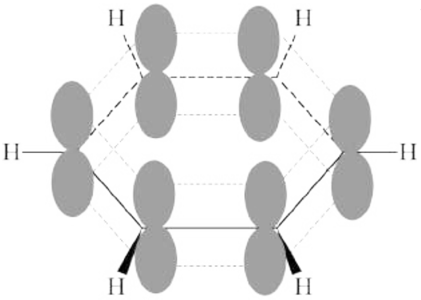
Bond lengths and angles in benzene

The hybrid structure is represented by inscribing a circle in the hexagon, and it is this new formula (III) that is most often used for benzene today. There are times, however, when an accounting of the electrons must be made, and for these purposes we may use one or the other of the Kekulé structures. We do this simply because the electron count in a Kekulé structure is obvious, whereas the number of electrons represented by a circle or portion of a circle is ambiguous. With benzene the circle represents the six electrons that are delocalized about the six carbon atoms of the benzene ring. With other systems, however, a circle in a ring may represent numbers of delocalized electrons other than six.



III

Resonance theory also tells us that whenever equivalent resonance structures can be drawn for a molecule, the molecule (or hybrid) is much more stable than any of the resonance structures would be individually if they could exist. In this way resonance theory accounts for the much greater stability of benzene when compared to the hypothetical 1,3,5-cyclohexatriene. For this reason the extra stability with benzene is called its resonance energy. It is this very large increment of resonance energy that places benzene and related compounds in a separate category that we call aromatic.

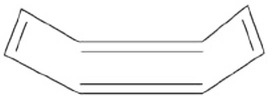


Huckel's Orbitals in benzene's orbital overlap is indicated by the dashed lines

Hückle's Rule: The (4n + 2)π Electron Rule: Hückel found that whether a cyclic hydrocarbon is aromatic or not depends on its number of π electrons. According to Hückel among, planar, monocylic fully conjugated polyenes only those possessing $(4n+2)\pi$ electrons, where n is a whole number will have special stability; that is be aromatic. In other words planar monocyclic rings with 2, 6, 10, 14, …, delocalised π-electrons should be aromatic.

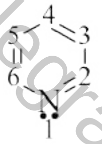
We can now understand why cyclobutadiene and cyclooctatetraene are not aromatic they are having a total of 4 and 8 π electrons respectively, both having an unpaired electron in each of two non bonding orbitals. Molecules with unpaired electrons are not usually stable; they are typically highly reactive and unstable.

Because cyclooctatetraene does not gain stability by becoming planar, it assumes the tub shape shown below (cyclooctatetraene would actually lose stability by becoming planar).

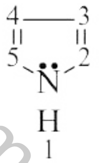


Cyclobutadiene belongs to a class of compounds called antiaromatic..

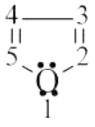
Heterocyclic compounds containing nitrogen, oxygen, or sulfur are by far the most common. Aromaticity is also shown by some heterocyclic compounds (some examples are shown below).



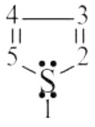
pyridine



pyrrole



furan



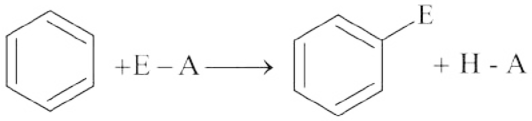
thiophene

Electrophilic Aromatic Substitution Reactions

Aromatic hydrocarbons are known generally as arenes. An aryl group is one derived from an arene by removal of a hydrogen atom, and its symbol is Ar —. Thus, arenes are designated ArH just as alkanes are designated RH.

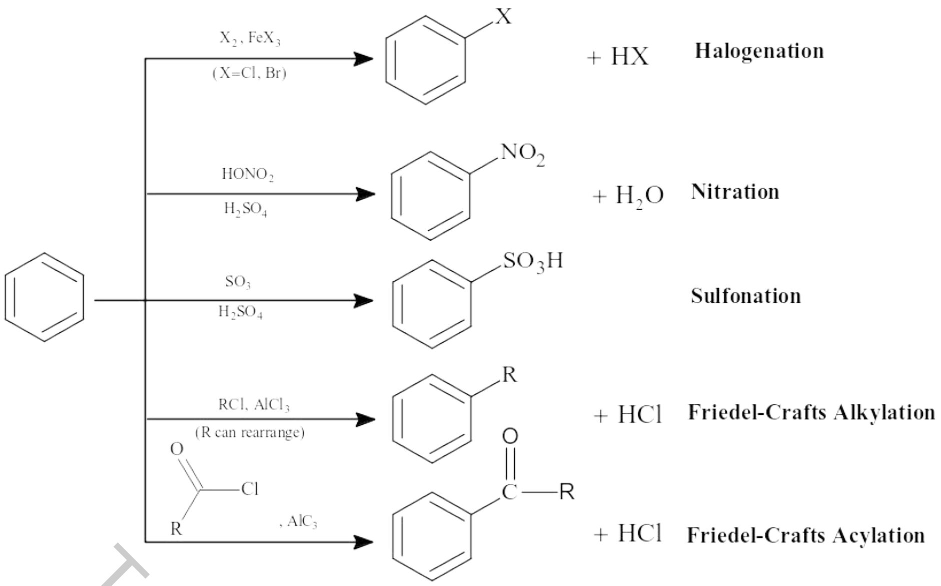
The most characteristic reactions of benzenoid arenes are the substitution reactions that occur when they react with electrophilic reagents. These reactions are of the general type shown below.

$$Ar - H + E - A \longrightarrow Ar - E + H - A$$



The electrophiles are either a positive ion (E^+) or some other electron-deficient species with a large partial positive charge. For example, benzene can be brominated when it reacts with bromine in the presence of $FeBr_3$. Bromine and $FeBr_3$ react to produce positive bromine ions, Br^+. These positive bromine ions act as electrophiles and attack the benzene ring, replacing one of the hydrogen atoms in a reaction that is called an electrophilic aromatic substitution(EAS).

Electrophilic aromatic substitutions allow the direct introduction of a wide variety of groups on an aromatic ring, and because of this they provide synthetic routes to many important compounds. The five electrophilic aromatic substitutions that we shall study in this chapter are outlined in figure.

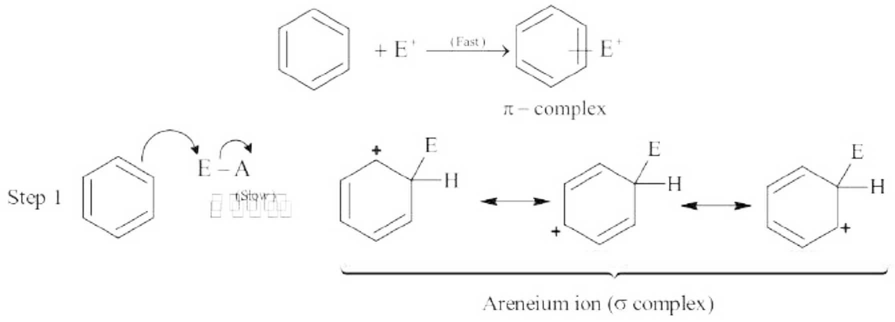


Electrophilic Aromatic Substitution Reactions

A General Mechanism for Electrophilic Aromatic Substitution: Benzene is susceptible to electrophilic attack primarily because of its exposed π electrons. In this respect benzene resembles an alkene, for in the reaction of an alkene with an electrophile the site of attack is the exposed π bond.

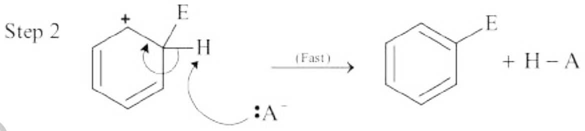
We see however, that benzene differs from an alkene in a very significant way. Benzene's closed shell of six π electrons gives it a special stability. So although benzene is susceptible to electrophilic attack, it undergoes substitution reactions rather than addition reactions. Substitution reactions allow the aromatic sextet of π electrons to be regenerated after attack by the electrophile has occurred. We can see how this happens if we examine a general mechanism for electrophilic aromatic substitution.

Once the electrophile, E^+ is generated in the reaction, it enters into some kind of a weak interaction with the π cloud of benzene ring leading to the formation of a π-complex. this π-complex is a donor-acceptor type of a complex, benzene being the donor and electrophile, the acceptor. These adducts are known as change transfer complexes. In the complex that benzene forms with bromine, it has been shown that the halogen molecule is located centrally and at right angles to the plane of the benzene ring.



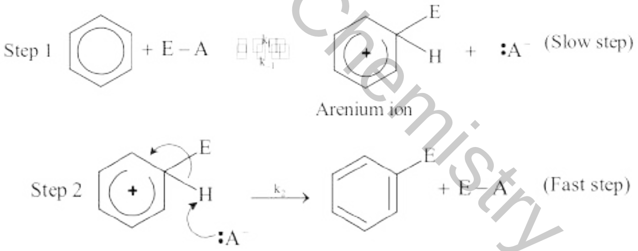
In step 1 the electrophile takes two electrons of the six-electron π system to form a σ bond to one carbon atom of the benzene ring. Formation of this bond interrupts the cyclic system of π electrons, because in the formation of the arenium ion the carbon that forms a bond to the electrophile becomes sp^3 hybridized and, therefore, no longer has an available p-orbital. Now only five carbon atoms of the ring are still sp^2 hybridized and still have p-orbitals. A calculated electrostatic potential map for the arenium ion formed by electrophilic addition of bromine to benzene indicates that positive charge is distributed in the arenium ion ring (figure) just as was shown in the contributing resonance structures.

In step 2 a proton is removed from the carbon atom of the arenium ion that bears the electrophile. The two electrons that bonded this proton to carbon becomes a part of the π system. The carbon atom that bears the electrophile becomes sp^2 hybridized again, and a benzene derivative with six fully delocalized π electrons is formed. We can represent step 2 with any one of the resonance structures for the arenium ion.



(The proton is removed by any of the bases present, for example, by the anion derived from the electrophile).

Kekulé structure are more appropriate for writing mechanisms such as electrophilic aromatic substitution because they permit the use of resonance theory, it can be described however, using the modern formula for benzene in the following way



Where k_1 and k_{-1} is the rate constant of the forward and backward reactions in step-1, k_2 is the rate constant of the step-2.

Nitration

Nitration reaction is generally carried out with a mixture of concentrated nitric acid and sulphuric acid. The reagents which cause nitration are called nitrating agents.

The various nitrating agents which are commonly employed are:

1. N_2O_5 in CCl_4 in the presence of P_2O_5 is used when anhydrous conditions are required.

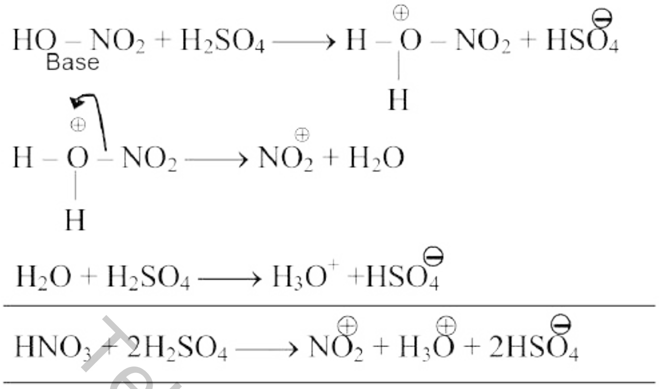
2. Ethyl nitrate ($C_2H_5ONO_2$) is used to carry out nitration in alkaline medium.

3. In the case of polycyclic hydrocarbons N_2O_4 and nitronium salts such as $NO_2^+ BF_4^-$ $NO_2^+ PF_6^-$, $NO_2^+ SO_3^-$ can be used. The electrophile involved in nitration reaction is nitronium ion $(NO_2^{\oplus})$.

Mechanism

1. Generation of electrophile from nitrating agent:

   a) In a mixture of nitric acid and sulphuric acid, an acid base reaction takes place in which nitric acid acts as the base.



$$\underset{\text{Base}}{HO}-NO_2 + H_2SO_4 \longrightarrow H-\underset{H}{\overset{\oplus}{O}}-NO_2 + HSO_4^{\ominus}$$

$$H-\underset{H}{\overset{\oplus}{O}}-NO_2 \longrightarrow \overset{\oplus}{N}O_2 + H_2O$$

$$H_2O + H_2SO_4 \longrightarrow H_3O^+ + HSO_4^{\ominus}$$

$$HNO_3 + 2H_2SO_4 \longrightarrow \overset{\oplus}{N}O_2 + H_3\overset{\oplus}{O} + 2HSO_4^{\ominus}$$

   b) N_2O_5 in CCl_4 when used, results in a spontaneous dissociation reaction.

$$N_2O_5 \rightleftharpoons \overset{\oplus}{N}O_2 + NO_3^{\ominus}$$

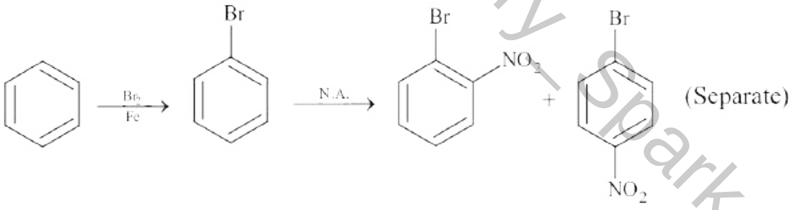
   c) With concentrated HNO_3 alone

$$2HNO_3 \rightleftharpoons NO_2^{\oplus} + NO_3^{\ominus} + H_2O$$

   The electrophile generated in this case is obtained by the behaviour of one nitric acid as the base and other molecule as the acid, but the equilibrium lies in the reactant side

Illustration 1: Convert benzene ⟶ p-bromonitrobenzene

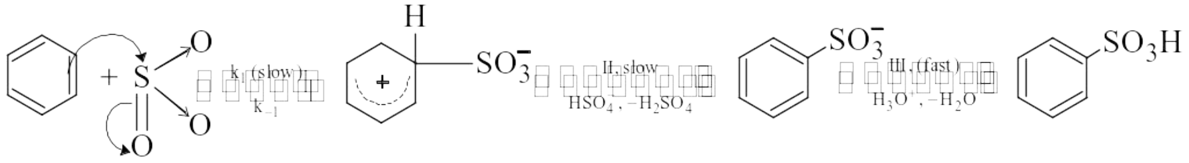
Solution:



Sulphonation

Sulphonation is another synthetically important reaction. It is often accomplished with concentrated sulphuric acid or fuming sulphuric acid containing excess of SO_3 or chlorosulphonic acid, $ClSO_2OH$.

It is believed that the electrophile varies with the reagent, though in all cases SO_3 is involved either free or along with a carrier, like in $H_3SO_4^+(SO_3 + H_3O^+)$ or $H_2S_2O_7$. Sulphur trioxide is generated from sulphuric acid as follows $2H_2SO_4 \rightleftharpoons HSO_4^- + H_3O^+ + SO_3$. The mechanism of sulphonation of benzene is given below:



Sulphonation is different from other aromatic electrophilic substitution reactions. Firstly, it is reversible and secondly, it shows some amount of isotope effect which is totally absent in other cases.

Halogenation

Halogenation of an aromatic ring is a synthetically important reaction. It takes place in the presence of varied reaction condition depending on the reactivity of the aromatic ring. For very reactive aromatic compounds in polar solvents, the molecular halogens themselves may acts as electrophiles. In the case of nonpolar solvents,halogenation is catalysed by a Lewis acid like $AlCl_3$, or $FeCl_3$, Reactivity of halogens has the following order,

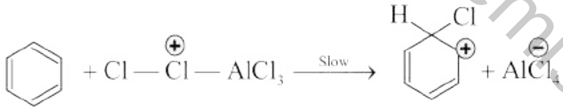
$$I_2 < Br_2 < Cl_2$$

Let us take chlorination as a representative reaction to understand the mechanism of halogenaton. Chlorine, in the presence of $AlCl_3$ or $FeCl_3$ forms a complex, $Cl_2 - AlCl_3$. This complex can itself be the reactive electrophile or it may dissociate to give Cl^+.

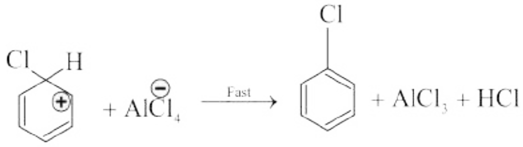
Step: 1

$$Cl-\overset{\bullet\bullet}{Cl}: + \underset{(anhydrous)}{AlCl_3} \rightleftharpoons Cl-\overset{\oplus}{Cl}-\overset{\ominus}{AlCl_3} \rightleftharpoons Cl^+ + AlCl_4^-$$

Step: 2



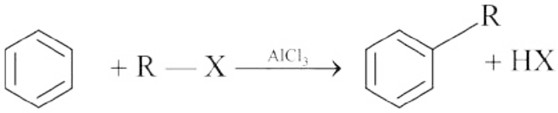
Step : 3



Friedel-Crafts Alkylation

Alkyl halides react with benzene in presence of aluminium chloride to yield alkyl benzenes. Alkylation of benzene with alkyl halides in the presence of aluminium chloride was discovered by Charles Friedel and James. M. Crafts in 1877.

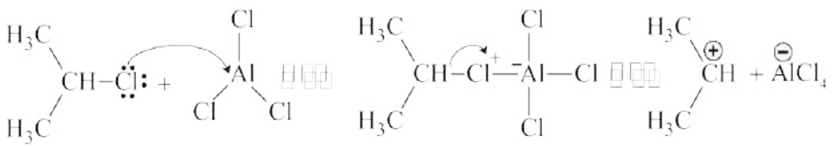
A general equation for a Friedel - Crafts alkylation reaction is the following.



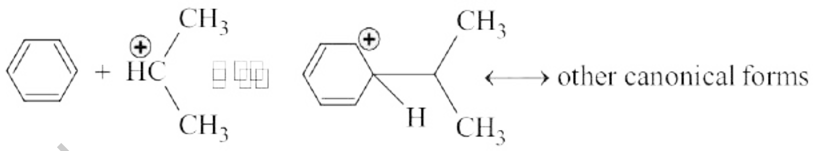
Alkyl halides by themselves are insufficiently electrophilic to react with benzene. $AlCl_3$ serves as a Lewis acid catalyst to enhance the electrophilicity of the alkylating agent. The mechanism for the reaction (shown in the following steps, with isopropyl chloride as R–X) starts with the formation of carbocation (step I). The carbocation then acts as an electrophile (Step–II) and attacks the benzene ring to form an arenium ion. The arenium ion (Step III) then loses a proton to generate isopropyl benzene. Some times carbocation rearrange to a more stable carbocation.

Mechanism

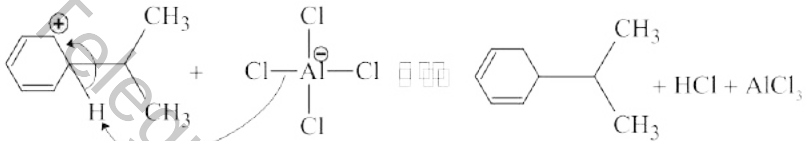
Step I



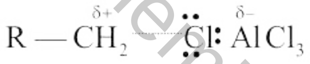
Step II



Step III



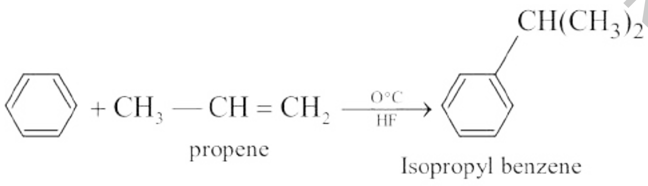
with R–X is a primary halide, a simple carbocation probably does not form. Instead, the $AlCl_3$ forms a complex with the alkyl halide and this complex acts as the electrophile. In the complex the carbon halogen bond is nearly broken and one in which the carbon atom has a considerable +ve charge.



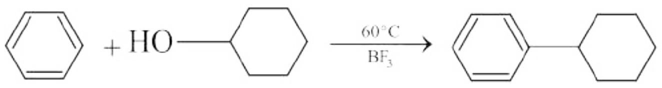
$$R-\overset{\delta+}{CH_2}\cdots\ddot{\underset{..}{Cl}}:\overset{\delta-}{AlCl_3}$$

These complexes are so carbocation like that they also undergo typical carbocation rearrangements.

Friedel-Crafts alkylations are not restricted to the use of alkyl halides and $AlCl_3$. Many other pairs of reagents that form carbocations (or carbocation like species) may be used as well. These possibilities include the use of a mixture of an alkene and an acid.



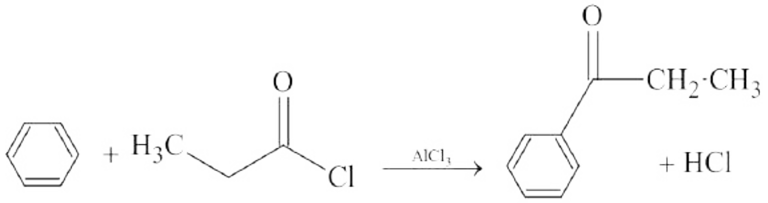
A mixture of an alcohol and an acid may also be used.



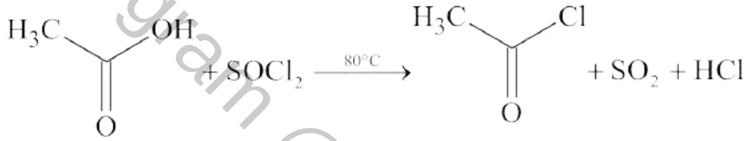
Friedel-Crafts Acylation

The group is called an acyl group and a reaction whereby an acyl group is introduced into a compound is called an acylation reaction.

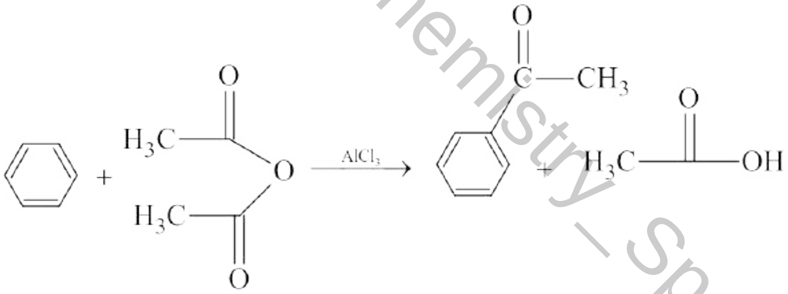
The Friedel-Crafts acylation reaction is an effective means of introducing an acyl group into an aromatic ring. The reaction is often carried out by treating the aromatic compound with an acyl halide.



Acyl chlorides (also called acid chlorides) are early prepared by treating carboxylic acids with thionyl chloride ($SOCl_2$) or phosphorous pentachloride (PCl_5).



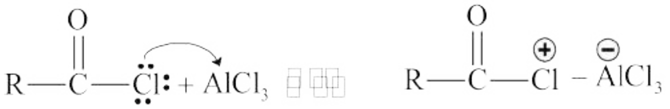
Friedel-Crafts acylations can also be carried cut using carboxylic acid anhydrides. eg.



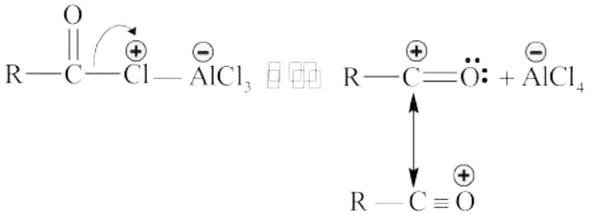
Mechanism

In most Friedel-Crafts acylation reactions the electrophile appears to be an acylium ion formed from an acyl halide in the following way.

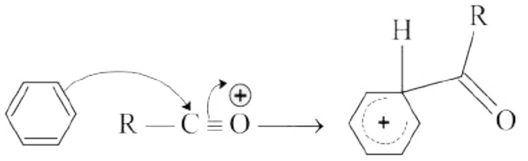
Step I



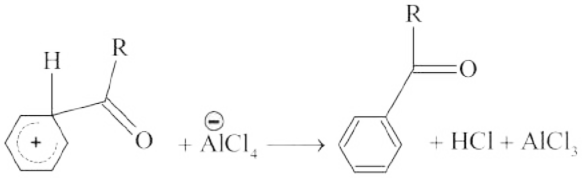
Step II



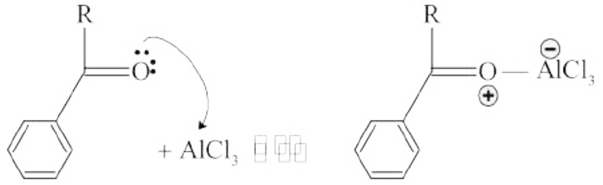
Step III



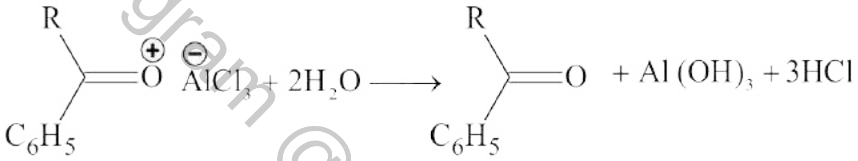
Step –IV



Step-V



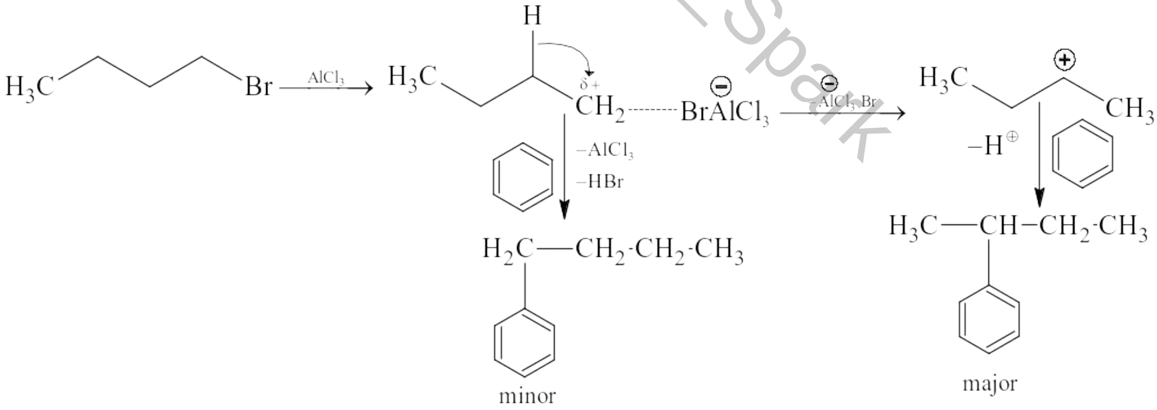
In the last step, $AlCl_3$ (a Lewis acid) forms a complex with the ketone (a Lewis base). After the reaction is over, treating the complex with water liberates the ketone.



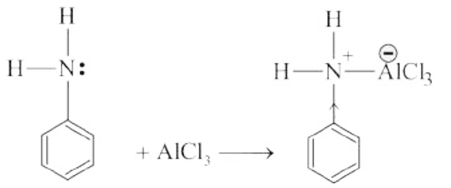
Limitations of Friedel - Crafts Reactions

Several restrictions limit the usefulness of Friedel-Crafts reactions.

1. When the carbocation formed from an alkyl halide, alkene, or alcohol can rearrange to a more stable carbocation, it usually does so, and the major product obtained from the reaction is usually the one from the more stable carbocation.

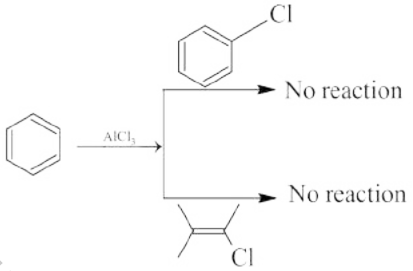


2. An aromatic ring less reactive than that of halobenzene don't undergo Friedal Craft's reaction. Aromatic ring containing - NH_2, $-NHR, -NR_2$, groups does not undergo friedal craft's alkylation due to formation of anilinum complex which is meta directing and has more electron withdrawing power than halogen in benzene ring.

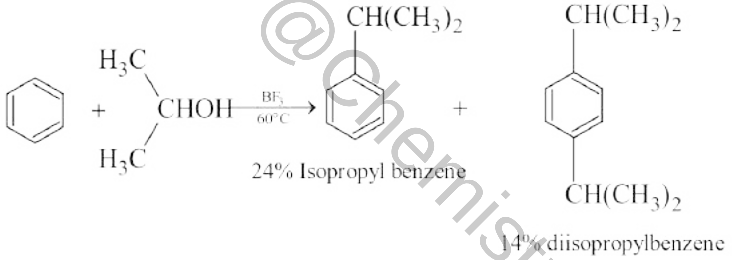


meta directing group and does not go Friedal Craft's reaction

3. Aryl and Vinylic halides cannot be used as the halide component because they do not form carbocations readily.

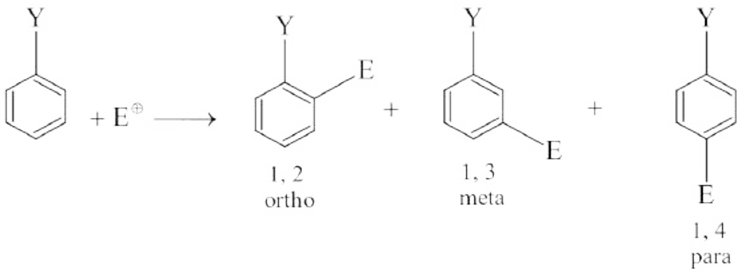


4. Polyalkylations often occur - Alkyl groups are electron releasing groups, and once one is introduced into the benzene ring it activates the ring towards further substitution.

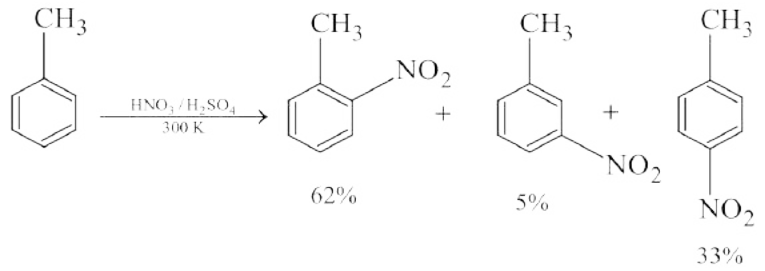


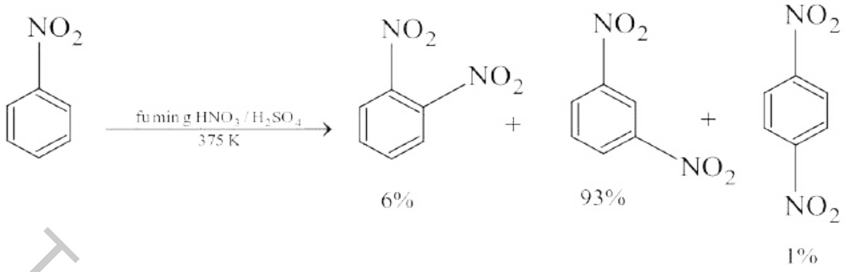
Orientation and Reactivity in Electrophilic Aromatic Substitution

In the case of benzene we get just one monosubstituted product in electrophilic aromatic substitution as all the positions are equivalent. However, for substitution in a compound which already has a group attached to the ring, three disubstituted products, (1,2), (1,3), (1,4) commonly called ortho, meta and para meaning next to, between and opposite respectivey are possible. These are abbreviated as o, m and p.

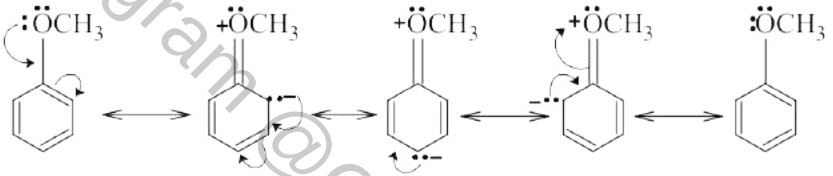


One may think, are all the three products formed in equal amounts or is there some kind of preference? Let us take two examples.



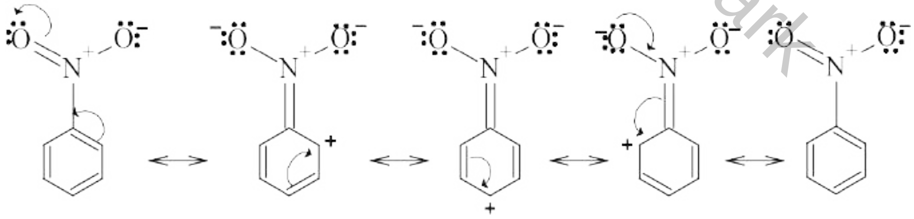


Donation of electrons into a benzene ring by resonance



If a substituent is attached to the benzene ring by an atom that is doubly or triply bonded to a more electronegative atom, the π electrons of the ring can be delocalized on to the substituent. Such substituents are said to withdraw electrons by resonance. Substituents such as —C=O, —C≡N, and NO_2 withdraw electrons by resonance. These substuents also withdraw electrons inductively because the atom attached to the benzene ring is more electronegative than a hydrogen.

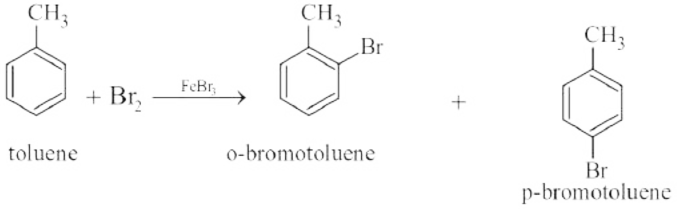
Withdrawal of electrons from a benzene ring by resonance



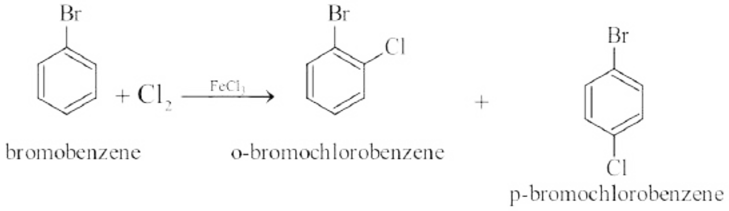
Notice the difference in the electron densities of the benzene rings in the electrostatic potential maps for anisole and nitrobenzene.

The substituent already attached to benzene determines the location of the new substituent. There are two possibilities - a substituent will direct an incoming substituent either to the ortho and para positions or will direct an incoming substituent to the meta position. All activating substituents and the weakly deactivating halogens are ortho/para directors, and all substituents that are more deactivating than the halogens are meta directors.

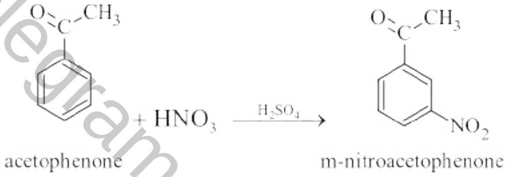
1. All activating substituents direct an incoming electrophile to the ortho and para positions.

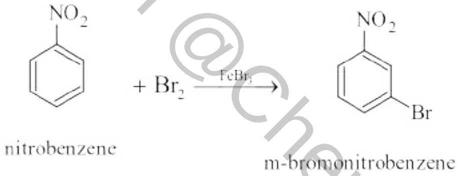


2. The weakly deactivating halogens also direct an incoming electrophile to the ortho and para positions.

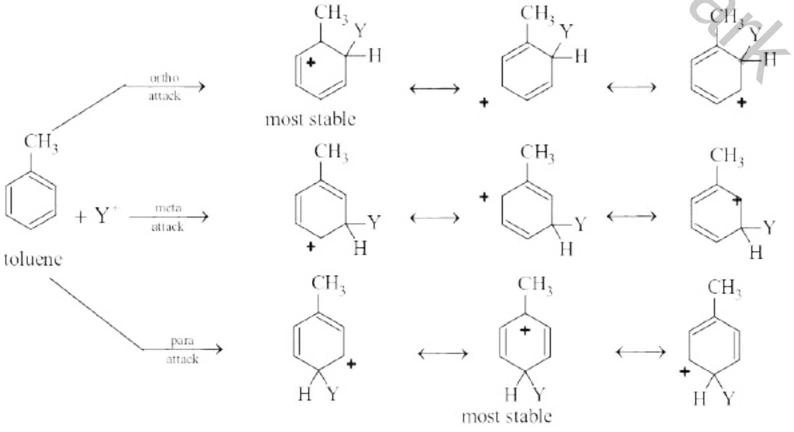


3. All moderately deactivating and strongly deactivating substituents direct an incoming electrophile to the meta position.

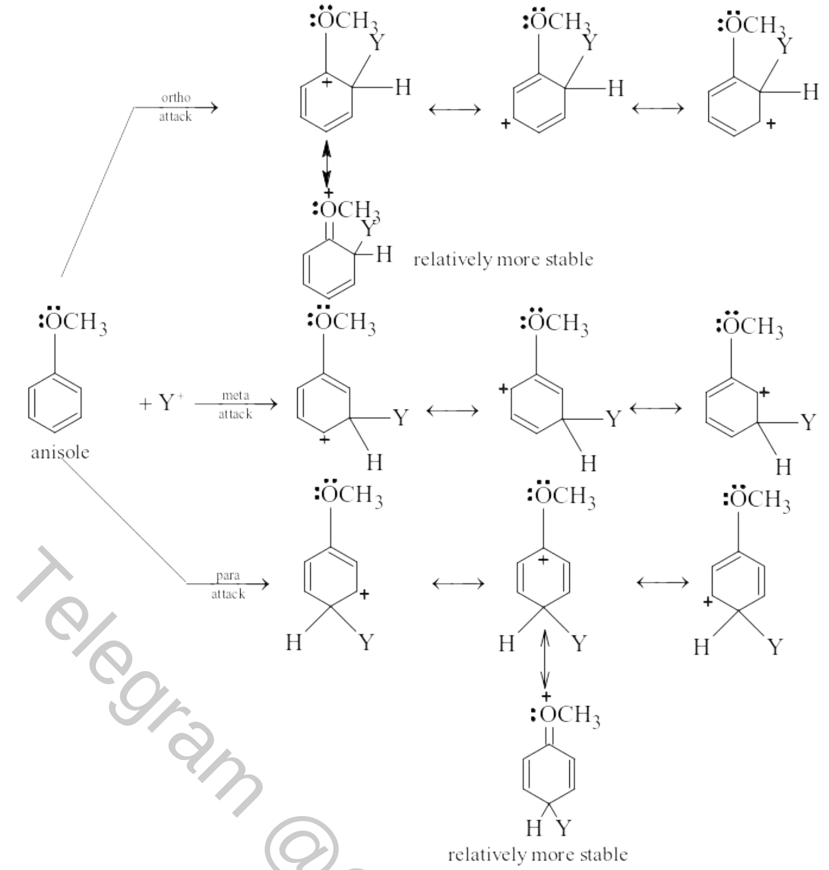




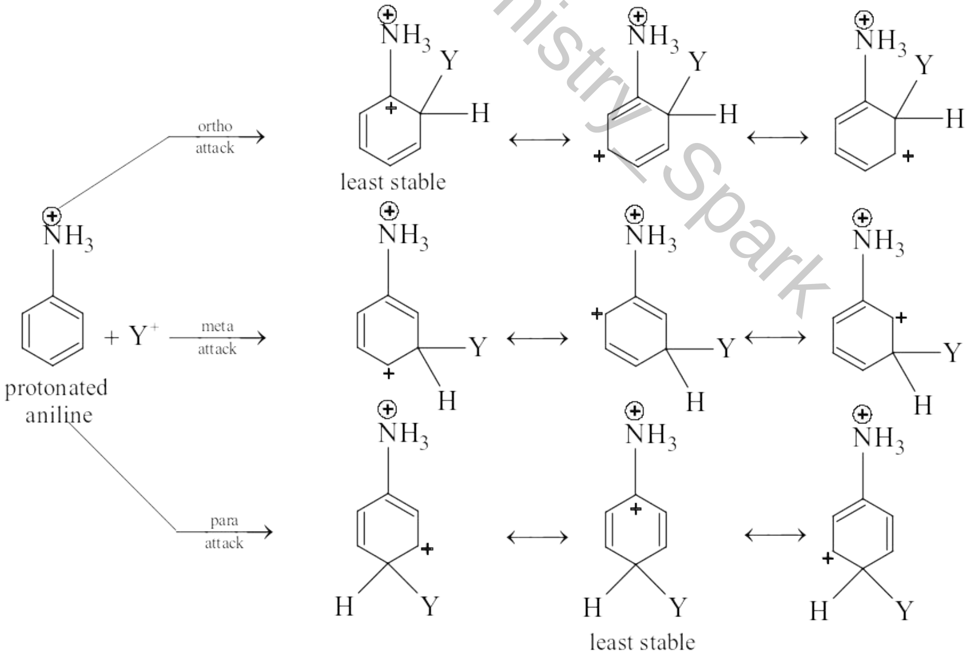
To understand why a substituent directs an incoming electrophile to a particular position, we must look at the stability of the carbocation intermediate formed in the rate-determining step. When a substituted benzene undergoes an electrophilic substitution reaction, three different carocation intermediates can be formed. Which one is more likely to be formed depends on their relative stabilities. Comparing the relative stabilities of the three carbocations allow us to determine the preferred pathway of the reaction because the more stable the carbocation, the less energy required to make it.



The structure of the carocation intermediates formed from the reaction of an electrophile with toluene at the ortho, meta, and para positions.

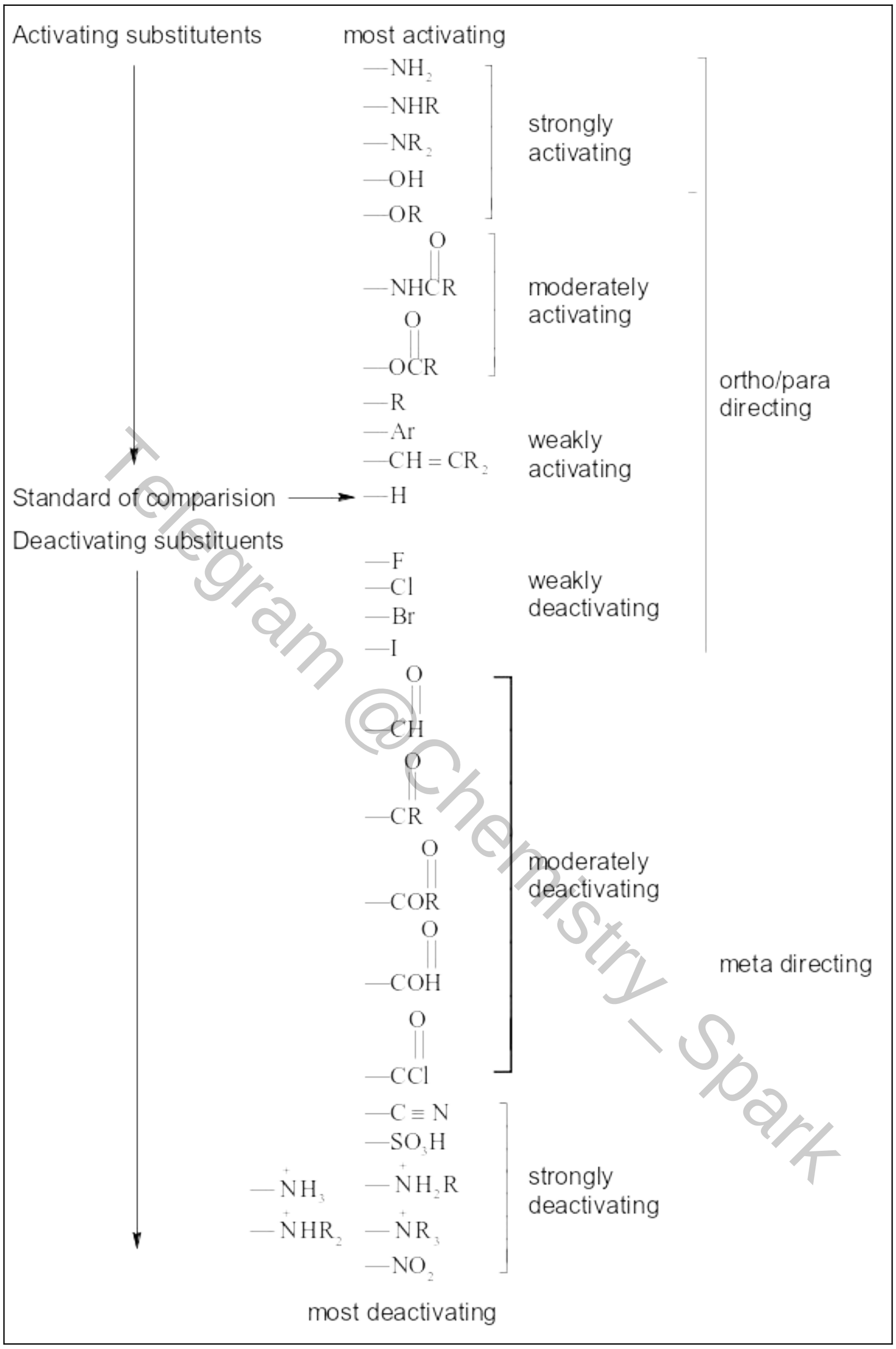


The structure of the carbocation intermediates formed from the reaction of an electrophile with anisole at the ortho, meta, and para positions.



The structures of the carbocation intermediates formed from the reaction of an electrophile with protonated aniline at the ortho, meta, and para positions.

The effect of substituents on the reactivity of a benzene ring toward electrophilic substitution



Ortho / Para Ratio

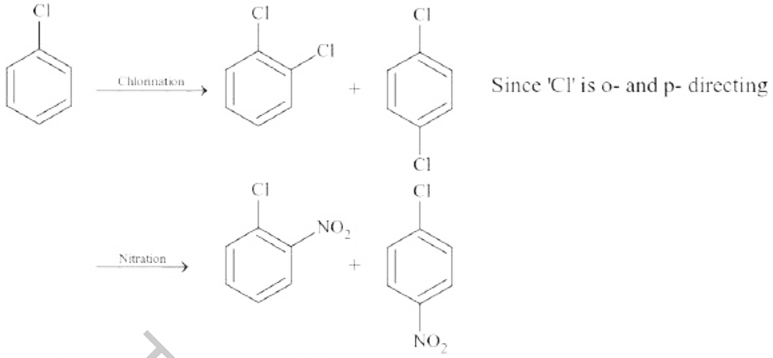
Directive influence of the groups during substitutions in benzene ring

a) The position of new incoming group (guest) in C_6H_6 nucleus is decided by the group already present in nucleus (host). This is known as directive influence of the host group present in the nucleus.

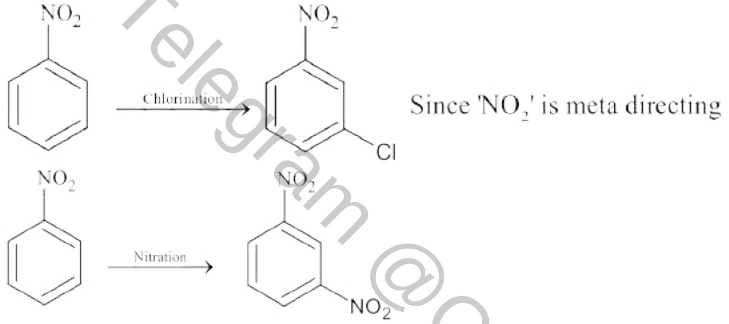
b) Directive influence of the host group is of two types i.e. the group already present in nucleus during further substitution of a group acts as

i) either ortho and para directing nature

ii) or meta directing nature



Since 'Cl' is o- and p- directing



Since 'NO$_2$' is meta directing

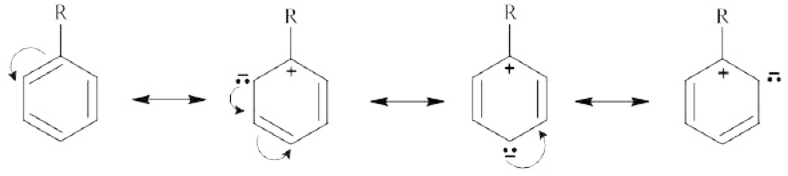
c) On the basis of their directive influence, the substituents have been classified as:

'o'- and 'p'- directing groups: $–NH_2$, $–NHR$, $–NR_2$, –OH, –OR, –SH, –SR, $–CH_3$, $–CH_2R$, $–CHR_2$, $–CR_2$, $–C_6H_5$, –Cl, –Br, –I, $–CH_2OH$, $–CH_2Cl$, $–CH_2NH_2$, $–CH_2CN$, $–CH_2COOH$, –CH = CH – COOH

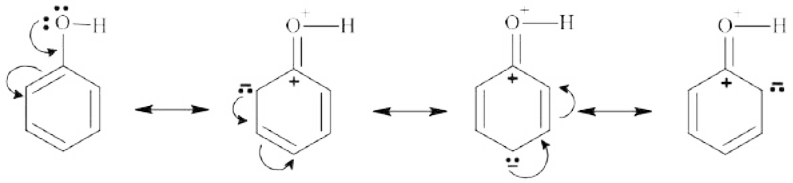
'm'-directing groups: $–NO_2$, $–SO_2H$, $–SO_2Cl$, –CHO, –COOH, –COOH, –COCl, –COOR, –COR, –COCOOH, $–CCl_3$, $–N^+H_3$, $–N^+H_2R$, $–N^+R_3$

Mechanism of o and p-directing groups: The o- and p-directing groups (except alkyl and $COO^–$) have unshared pair of electrons on the atom attached on benzene nucleus. The mechanism is therefore discussed in terms of two aspects.

Mechanism of o- and p-directing groups not have unshared pair of electrons: Consider an alkyl group attached on C_6H_6 nucleus. It is an electron repelling group. The +I.E. of alkyl group and + Electromeric effect along with + Mesomeric effect give rise to an increase in electron density at o- and p-positions and thus provide site for electrophile to attack these centres. This can also be explained in terms of hyperconjugation.

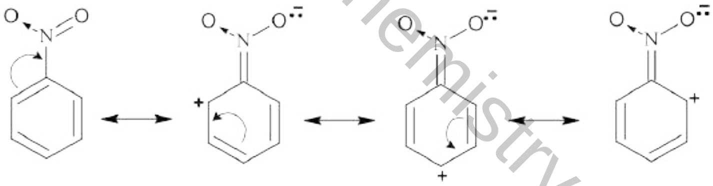


Mechanism of o- and p-directing gps having unshared pair of electron(s): Consider –OH group attached on C_6H_6 nucleus having two unshared pair of electron on O atom. One of the such unshared pair of electron shifts towards nucleus following +E effect and +M effect and give rise to an increase in electron density at o- and p-position and thus provide seat for electrophile to attack these centres.



Note:
1. ***A free electron pair charge or increased density at o- and p-position activates ring for further substitution. That is why nucleus having o- and p-directing groups are more reactive than benzene for S_E reactions.***
2. ***The o- and p-directing groups (except halogens) are thus also known as activating groups.***
3. ***Halogens, although increase electron density at o- and p- positions due to +E and +M effect, but they also deactivate the ring due to strong –I effect. (Halogens are strong electron withdrawing groups).***

Mechanism of m-directing groups: The m-directing groups except CCl_3, either possess a –ve charge or the atom of such group attached to nucleus has a multiple bond on it. The –E, –M and –I effect of all such groups leading the displacement of the electrons away from the nucleus and withdraw the electron from o- and p-position, thereby producing a decrease in electron density at o- and p-position.

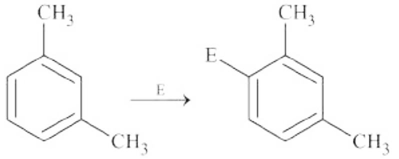


The electron density at meta position remains unchanged, however, the relative electron density at meta position becomes more and thus electrophile attacks m-positions in all such cases.

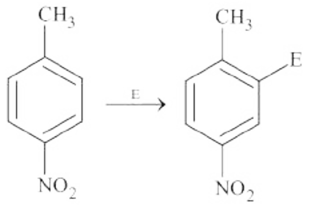
Note:
1. ***The meta position electron density remains unaffected in presence of m-directing groups and thus these groups provide no extra facility for electrophile. On the country they deactivate the ring for further substitution. That is why presence of m-directing group on benzene nucleus give rise to S_E reactions with difficulty in comparison to benzene itself.***
2. ***–CCl_3, $-NH_3^+$ and NR_3^+ groups undergo –I effect followed with –M effect.***

Competitive orienting effect of two substituents

1. ***Two groups reinforce (provide same place for S_E reaction) each other***

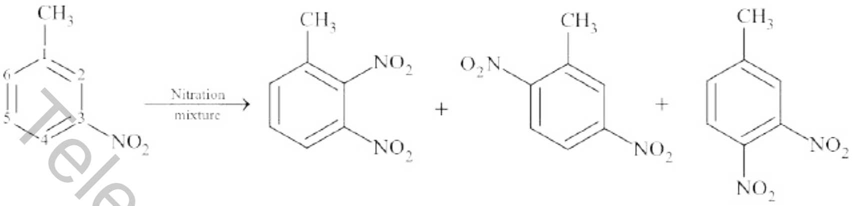


Electrophilic attacks o- and p- positions of each CH_3 group, which are same and only one possible product is formed.

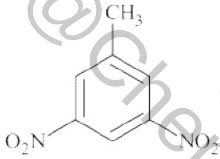


Electrophile attacks o- and p-positions of CH_3 group and m-positions of $–NO_2$ group which are same and only one possible product is formed.

2. ***Two groups, one o- and p-directing and one meta directing provides different positions for S_E reactions:*** The o- and p-directing group activates the ring by supplying electrons at o- and p-positions, whereas m-directing group deactivates ring by withdrawing electrons from o- and p-positions. In such cases the power of o- and p-directing group overpowers the m-directing group e.g.

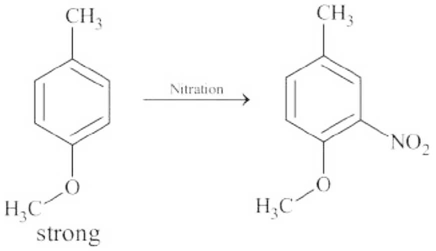


CH_3 group supplies electrons to 2,6 and 4 positions; NO_2 withdraws electrons from 2,6,4 positions. The power of CH_3 group predominates and no substitution occurs at m-position of $–NO_2$ group i.e.



is not formed

3. **Two o- and p-directing groups – one is strong activating and other one is weak:** The o- and p-directing group having strong nature to supply electron pair and o- and p-position overpowers the effect of other o- and p-directing group having weak nature to supply electron pair at o- and p-position e.g. OCH_3 is relatively stronger o- and p-directing group than methyl group and thus substitution occurs with respect o- and p-positions of OCH_3 group.



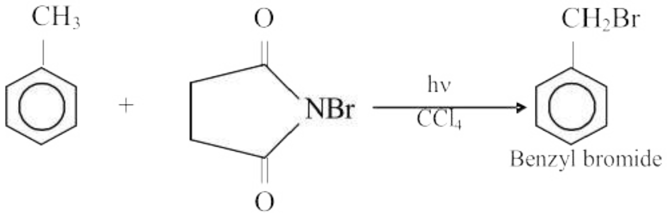
Note: ***1. p-position is not vacant for OCH_3 group and thus only at o-position substitution occurs.***

2. No substitution at o-position of CH_3 group.

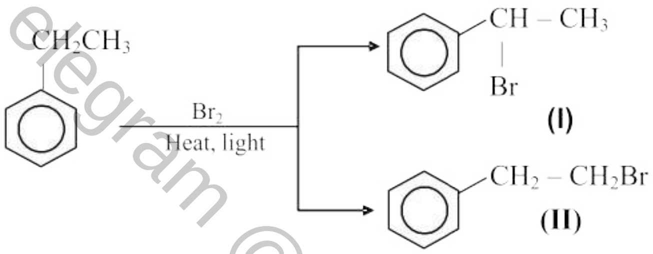
4. **Two weak activating or deactivating groups or two strong activating or deactivating groups are present:** All possible isomers are formed.

Reactions of Alkyl Benzenes

Halogenation of the side chain: The side chain halogenation of alkyl benzenes takes place in the presence of light or high temperatures. Side chain halogenation is mostly carried out by using the reagent N-bromosuccinimide (NBS) in the presence of light.



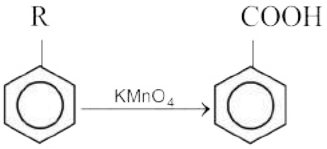
An alkyl benzene with side chain other than methyl may lead to the formation of more than one products.



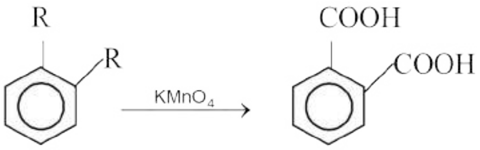
Order of stability of free-radials.

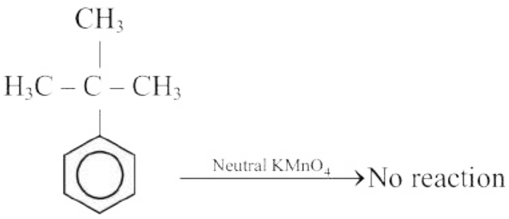
Allyl > Benzyl > 3° > 2° > 1° > CH_3 ≈ vinyl (from bond dissociation energy data).

Oxidation of side chain: Although benzene itself is not susceptible to oxidation but side chain attached to the benzene ring undergoes oxidation and converts itself into a –COOH group. Oxidation of side chain takes place after substance is heated for a long time with $KMnO_4$.



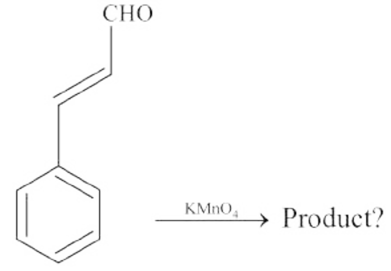
The above reaction can be used for identifying substitution pattern in aromatic compound. If any compound gives pthalic acid on heating with $KMnO_4$, then we can infer that it is ortho disubstituted benzene.



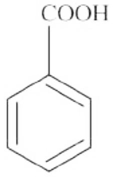


There is no reaction because of the absence of a benzylic hydrogen.

Illustration 2: Find the product



Solution:



Concepts Review

Exercise 1: ***o- and m-chlorophenols have different boiling points. Explain.***

Solution: o-chlorophenol shows intramolecualr H-bonding, whereas m-chlorophenol shows intermolecular H-bonding. The later is stronger one and thus boiling point of m-chlorophenol is more than o-chlorophenol.

Exercise 2: ***Explain why o-hydroxy benzaldehyde is liquid at room temperature while p-hydroxy benzaldehyde is a high melting solid.***

Solution: The former shows intramolecular H-bonding.

Exercise 3: ***Benzene is highly unsaturated but it does not give electrophilic addition reactions. Explain***

Solution: Because it loses aromaticity.

Exercise 4: ***Is benzene the same as 1,3,5-cyclohexatriene?***

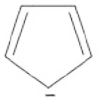
Solution: No. In benzene all the six bonds are of identical length (1.40Å) on account of resonance, but in 1,3,5-cyclohexatriene a hypothetical molecule the bond lengths are 1.54Å and 1.34Å alternatively.

Exercise 5: ***Nitrobenzene, but not benzene is used as a solvent for the Friedel-Craft alkylation of bromobenzene.***

Solution: During alkylation of bromobenzene, if benzene is used as solvent, alkylation of benzene will take place because benzene is more reactive for S_E reactions than bromobenzene. On the other hand, nitrobenzene does not undergo Friedel-Craft reaction and can be used as solvent for alkylation of bromobenzene.

Exercise 6: ***The pK_a for cyclopentadiene is 16 and that of cycloheptatriene is 36.***

Solution: Cyclopentadiene is more acidic because its conjugate base, cyclopentadienyl anion is unusually stable due to aromatic character,



This is delocalized and give rise to a ring with six delocalized π electrons.

Exercise 7: ***Nitrobenzene does not undergo Friedel – Craft's alkylation.***

Solution: The nitro group in nitrobenzene strongly deactivates the benzene ring. This decreases the reactivity of benzene towards Friedel – Craft's alkylation.

Exercise 8: ***Aniline undergoes bromination in ortho and para position but in presence of strong acid it gives m-bromo aniline. Explain?***

Solution: $-NH_2$ group is o– and p-directing. However, in presence of strong acid aniline combines with proton to form $C_5H_5\overset{+}{N}H_3$ and $-\overset{+}{H}N_3$ group is m-directing. thus, m-bromo product is formed in presence of strong acid.

Exercise 9: ***Friedel Crafts acylation requires an excess of the catalyst but Friedel Craft's alkylation requires only a catalytic amount. Explain.***

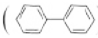
Solution: The product of acylation co-ordinates with the catalyst and removes the latter from the reactant side. For this reason Friedel crafts acylation requires an excess of catalyst. The product of alkylation does not coordinate with the catalyst. So, the catalyst can form complex with the alkylation agent and the catalyst propagates the reaction.

Exercise 10: ***Aniline doesnot undergo Friedel Craft alkylation reaction. Why?***

Solution: Due to Lewis acid base reaction, $-NH_2$ group become ring deactivating.

Exercise 11: ***Benzene ring despite of unsaturated ring, undergoes electrophilic substitution rather than electrophilic addition, why?***

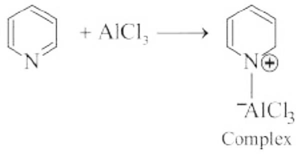
Solution: Since benzene is aromatic compound. Since on electrophilic addition, first of it forms σ-complex which is non-aromatic in nature or, in other words, on electrophilic addition, the aromaticity of the benzene ring gets ruptured. But on electrophilic substitution, the aromaticity of the ring remains retained.

Exercise 12: ***Ortho & Para product of the electrophilic substitution of diphenyl ring*** () ***is major, but the meta product is minor, why?***

Solution: When electrophile attacks, on ortho or, para position, the produced carbocation is more resonance stabilized due to more resonating structures. But when electrophile attacks on meta position, then produced carbocation is less resonance stabilized due to only, three resonating structures.
As we know that higher the stability of the carbocation produced, higher the stability of the product produced i.e. major the product. That's why ortho & para substitution product of diphenyl ring gives major product, and meta is minor product.

Exercise 13: ***Explain why pyridine does not undergo Friedel – Craft's reaction?***

Solution: The Lewis acids $AlCl_3$ or $FeCl_3$, used as catalyst in Friedel - Craft's reaction coordinate with nitrogen of the pyridine through lone pair of electrons and form a complex. The +ve charge on N greatly diminishes the reactivity towards electrophilic substation.



Solved Problems

Objective

Problem 1: In which of the following molecules, the substituent does not exert its resonance effect

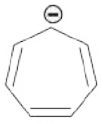
(a) $C_6H_5NH_2$ (b) $C_6H_5\overset{\oplus}{N}H_3$

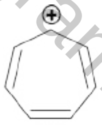
(c) C_6H_5OH (d) C_6H_5Cl

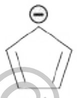
Solution: In $C_6H_5\overset{\oplus}{N}H_3$ there is no lone pair electrons on the N- atom and hence it cannot exert its resonance effect.

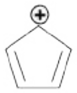
$\therefore$ **(b)**

Problem 2: Which of the following species would be expected to exhibit aromatic character?


(I)


(II)


(III)

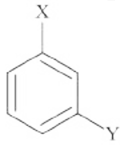

(IV)

(a) I and IV (b) II and IV
(c) I and III (d) II and III

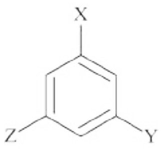
Solution: II and III have delocalized six π electrons and hence are aromatic.

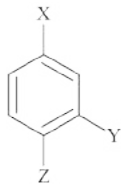
$\therefore$ **(d)**

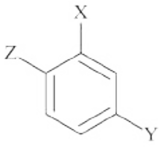
Problem 3: The compound



(where X is an O – P, directing group and Y is m-directing group)
is subjected to electrophilic substitution reaction for introduction of Z. The compound formed would be

(a) 

(b) 

(c) 

(d) Both (b) and (c)

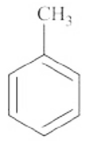
Solution: The orientation is decided by the activating group i.e. o, p- directing
∴ **(b) and (c)**

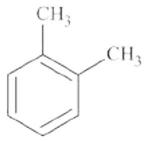
Problem 4: When Nitrobenzene is treated with Br_2 in presence of $FeBr_3$, the major product formed is m-bromonitro benzene. Statements which are related to obtain m-isomer are:

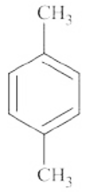
(a) The electron density on meta carbon is more than that on ortho and para positions.
(b) The intermediate carbonium ion formed after initial attack of Br^+ at the meta position is least destabilized.
(c) Loss of aromaticity when Br^+ attacks at the ortho and para positions not at meta position
(d) Easier loss of H^+ to regain aromaticity from the meta position than from ortho and para positions.

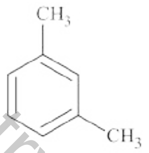
Solution: The intermediate carbonium ion formed after initial attack of Br^+ at the meta position is least destabilized.
∴ **(b)**

Problem 5: Terepthalic acid is obtained by oxidation of which of following compounds?

(a)


(b)


(c)


(d)


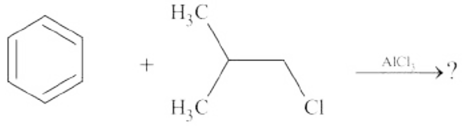
Solution: Terepthalic acid is a para dicarboxylic acid
∴ **(c)**

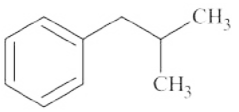
Problem 6: The most basic compound among the following is:

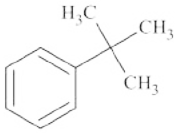
(a) Benzylamine (b) Aniline
(c) Acetaniline (d) p-nitroaniline

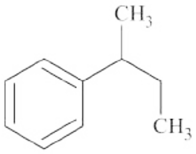
Solution: Rest all show less tendency to donate electron pair due to resonance.
∴ **(a)**

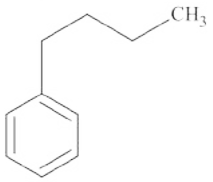
Problem 7: Which of the following is the major organic product of the following reaction?



(a) 

(b) 

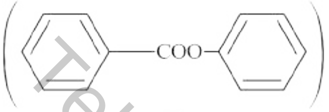
(c) 

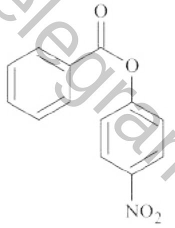
(d) 

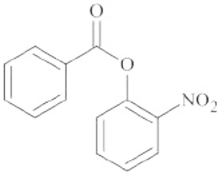
Solution: The product obtained by the more stable carbocation

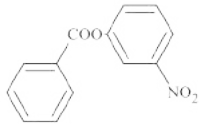
∴ **(b)**

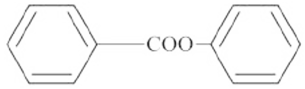
Problem 8: Which of the following is correct for the mononitration of phenyl benzoate?



(a) 

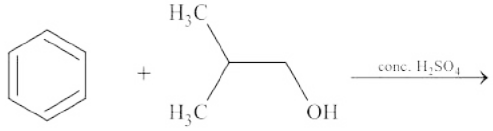
(b) 

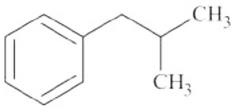
(c) 

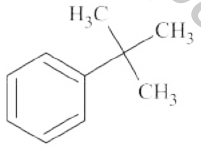
(d) 

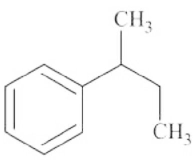
Solution: ∴ **(a)**

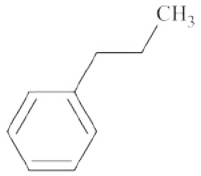
Problem 9: Which of the following is correct for the following reaction?



(a) 

(b) 

(c) 

(d) 

Solution: The isobutylium ion rearranges to give most stable t-butyl carbonium ion.

∴ **(b)**

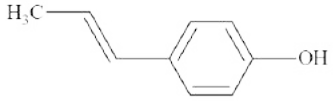
Problem 10: Arrange the following compounds in order of increasing dipole moment

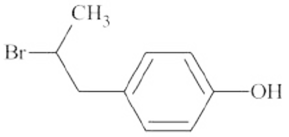
Toluene (I) m-dichlorobenzene (II)

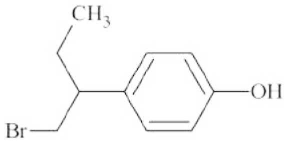
o-dicholrobenzene (III) p-dichlorobenzene (IV)

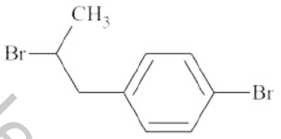
(a) I < IV < II < III (b) IV < I < II < III
(c) IV < I < III < II (d) IV < II < I < III

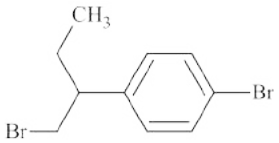
Solution: ∴ (b)

Problem 11: The reaction of  with HBr gives:

(a) 

(b) 

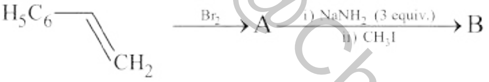
(c) 

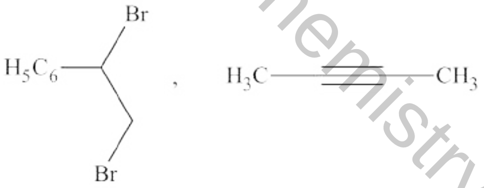
(d) 

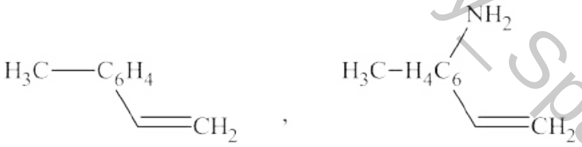
[DPMT 1997]

Solution: The benzylic carbocation is more stable.
∴ **(b)**

Problem 12: The products A and B in the following reaction sequence are:



(a) 

(b) 

(c) Both of the above
(d) None of the above

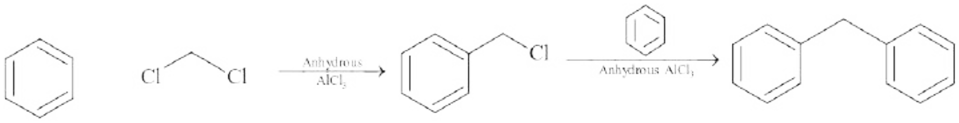
[MH CET 2000]

Solution: ∴ **(a)**

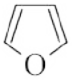
Problem 13: Which of the following structures correspond to the product expected, when excess of C_6H_6 reacts with CH_2Cl in presence of anhydrous $AlCl_3$.
(a) $(Ph)_2CHCl$ (b) $PhCHCl_2$
(c) Ph_2CCl_2 (d) Ph_2CH_2

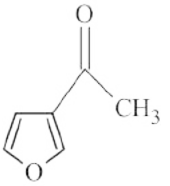
[MP PET 2002]

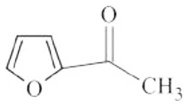
Solution:

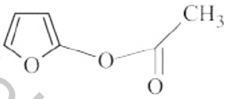


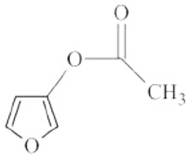
∴ (d)

Problem 14:  + $(CH_3CO)_2O \xrightarrow{BF_3} P$, P is

(a) 

(b) 

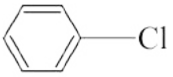
(c) 

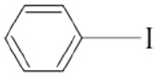
(d) 

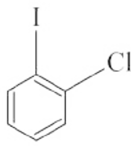
[UPSEAT 2003]

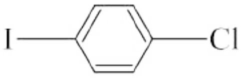
Solution: ∴**(b) Fridel-Craft acylation**

Problem 15: Benzene on reaction with ICl in presence of anhydrous $AlCl_3$ gives?

(a) 

(b) 

(c) 

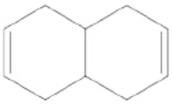
(d) 

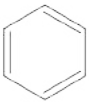
[RPET 1999]

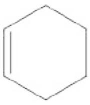
Solution: When ICl is heated with $AlCl_3$ $I^+ AlCl_4$ complex formation is more farourable than $Cl^+ AlCl_3I$ complex. So iodiobenzene is formed.

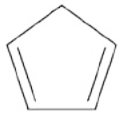
∴ **(b)**

Problem 16: Which of the following will show aromatic behaviour

(a) 

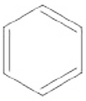
(b) 

(c) 

(d) 

[KCT 1996]

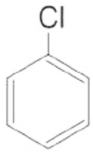
Solution: (b)



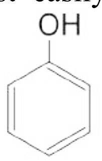
(1) molecule is planar.
(2) 6 π electrons are present.

Problem 17: Which of the following will be most easily attacked by an electrophile

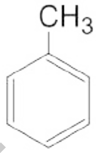
(a)



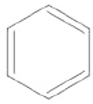
(b)



(c)



(d)



[MP PET 2004]

Solution: (b) Due to mesomeric effect (+M) of –OH group the electron density on benzene ring increase so the electrophile easily attacked on these electron rich center.

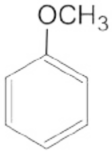
Problem 18: Which is an electrophile

(a) $AlCl_3$ (b) CN^-
(c) NH_3 (d) CH_3OH

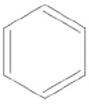
[DCE 2000]

Solution: (a) $AlCl_3$ is lewis acid i.e., electron deficient compound. So it is electrophile.

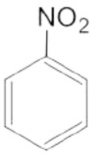
Problem 19: Among the following compounds (I – III) the correct order of reaction with electrophilic reagent is



(I)



(II)

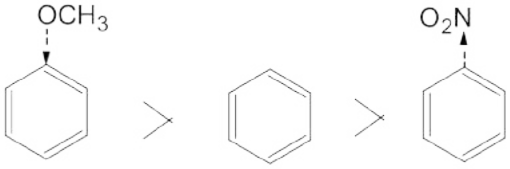


(III)

(a) II > III > I (b) III < I < II
(c) I > II > III (d) I = II > III

[CBSE (PMT) 1997]

Solution: (c)



Methoxy group is electron releasing it increases electron density of benzene nucleus while –NO_2 decreases electron density of benzene.

Problem 20: Cyclic hydrocarbon molecule ‘A’ has all the carbon and hydrogen in a single plane. All the carbon-carbon bonds are of same length less than 1.54 $\overset{0}{\text{A}}$, but more than 1.34 $\overset{0}{\text{A}}$. The C – C bond angle will be

(a) 109°28′ (b) 100°
(c) 180° (d) 120°

[BVP 2003]

Solution: (d) Molecule ‘A’ is benzene because in benzene bond length is between single and double bond.

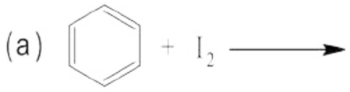
Problem 21: Toluene when treated with Br_2/Fe gives p-bromo toluene as a major product because –CH_3 group :

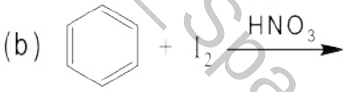
(a) is o and p-directing
(b) is m-directing
(c) activates the ring by hyperconjugation
(d) activates the ring by +R effect (resonance or measomeric effect)

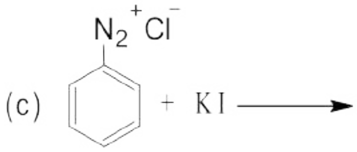
Solution: (a) and (c) explanation :

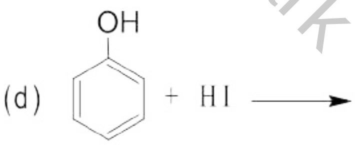
(a) is correct because – CH_3 group is electron releasing
(b) is wrong because – CH_3 is not electron withdrawing, so cannot be meta directing .
(c) is correct because –CH_3 has three C – H bonds due to which it activates the benzene ring by hyperconjugation
(d) is not correct because – CH_3 does not have lone pair of electrons.

Problem 22: Iodobenzene can be obtained by









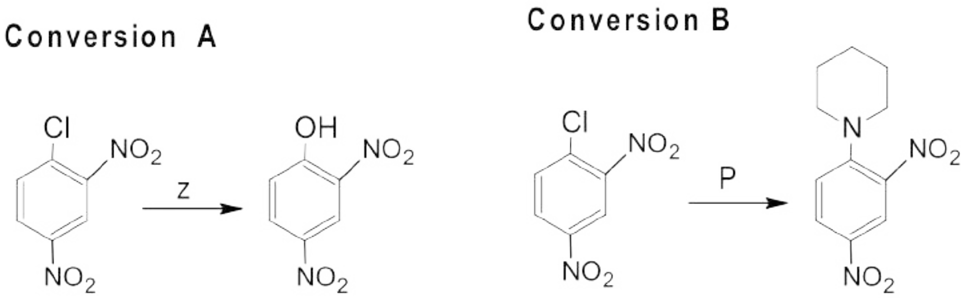
Solution: (b) and (c) explanation :

(a) is not possible because HI is good reducing agent, therefore, it will reduce iodobenzene back to benzene.
(b) is correct because HI will be oxidized to HIO_3 which will react with HI to form I_2 and water to slow down reversibility.
(c) is correct because benzene diazonium chloride is highly reactive and reacts with I^- to give iodobenzne.
[Note : HI above cannot be used in this reaction, it can be used along with Cu

powder (Gattermann reaction).

(d) is not possible because phenol does not undergo nucleophilic substitution reaction with HI.

Problem 23: For the following conversions

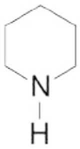


(a) For conversions A, the steps in Z (i) aq OH^-/Δ (ii) H^+/H_2O

(b) For conversion B, the steps in P (i) NH_3 + CuO/Δ
(ii) $Cl-CH_2CH_2CH_2-CH_2-CH_2-Cl$

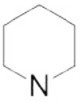
(c) For conversion A, the steps in Z (i) aq NaOH at – 1000^0C (ii) H^+/H_2O

(d) For conversion B, the steps in P (i)



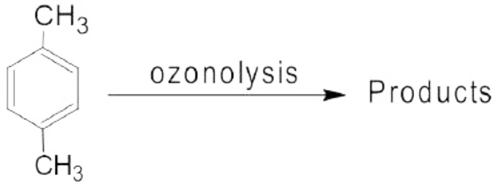
Solution: (a) and (b) Explanation : In conversion (A) due to the presence of strong deactivating groups chlorobenznen undergoes easily nucleophilic substitution reaction hence reagent NaOH or KOH is sufficient to provide HO^- with slight warming.

In conversion (B) again in nucleophile i.e. which is piperidine is



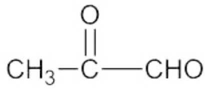
required as compound (B) can undergo easy nucleophilic substitution reaction Hence (a) and (d) are correct answers .

Problem 24:



The products formed are

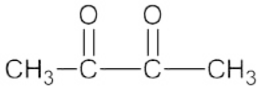
(a)



$CH_3-\overset{O}{\overset{\|}{C}}-CHO$

(b) CHO – CHO

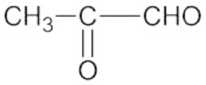
(c)



$CH_3-\overset{O}{\overset{\|}{C}}-\overset{O}{\overset{\|}{C}}-CH_3$

(d) HCOOH

Solution: (a) and (b) Explanation : CHO – CHO and are formed



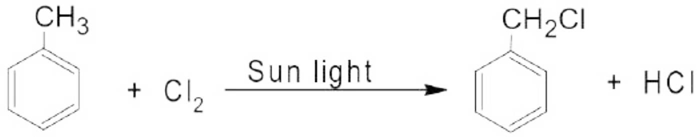
$CH_3-\underset{O}{\underset{\|}{C}}-CHO$

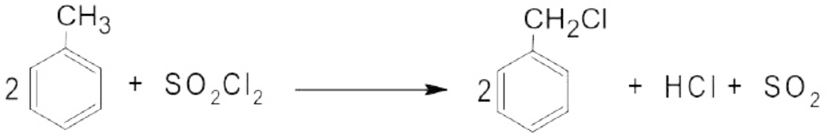
Problem 25: Benzyl chloride ($C_6H_5CH_2Cl$) can be prepared by chlorination with

(a) SO_2Cl_2 (b) Cl_2

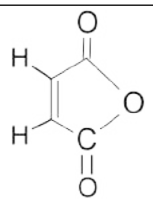
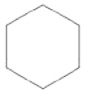
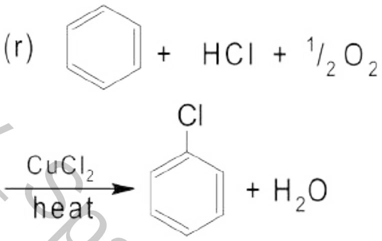
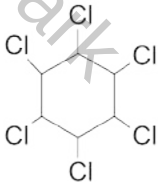
(c) $SOCl_2$ (d) NaOCl

Solution: (a) and (b) are correct





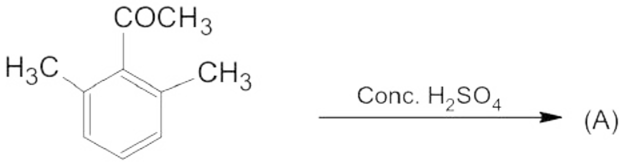
Problem 26: Matching the following

Column – I	**Column – II**
(a) Reaction of benzene with Cl_2 in presence of sunlight	(p) 
(b) Raschig process	(q) 
(c) Reaction of H_2 with benzene in presence of Ni as a catalyst at high temperature	(r) 
(d) Reaction of benzene with air in presence of V_2O_5 at 770K and heating strongly.	(s) 

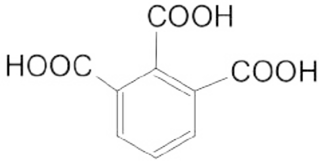
Solution: **(a - s), (b – r), (c – q), (d – p)**

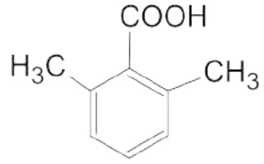
Write-up - I

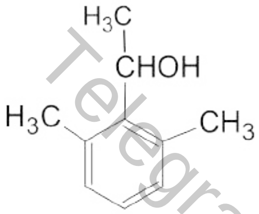
The typical reaction of benzene and other aromatic compounds are electrophilic substitution. Presence of electron donating group activates the ring towards electrophilic substitution, while presence of electron withdrawing group deactivates the ring towards electrophilic substitution but at the same time activates the ring towards nucleophilic substitution. Some groups are predominantly meta-directing and all of these are deactivating. Except halogen, most of the O– and P– directing groups are activating groups.

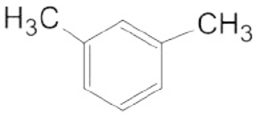
1. 

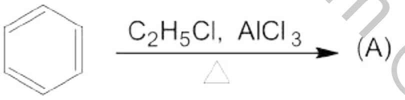
(A) is

(a) 

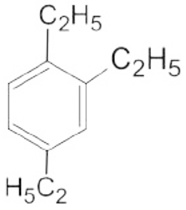
(b) 

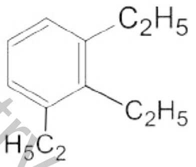
(c) 

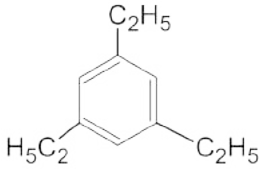
(d) 

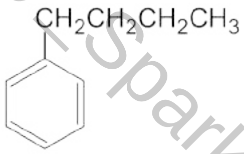
2. 

A is trisubstituted benzene. The structure of A is

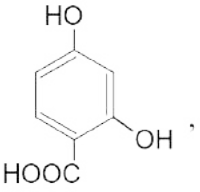
(a) 

(b) 

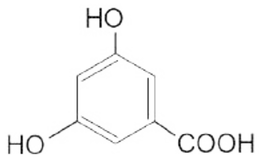
(c) 

(d) 

3. Among the three isomers shown below

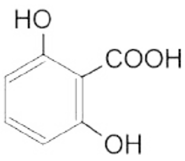


(I)



(II)

and

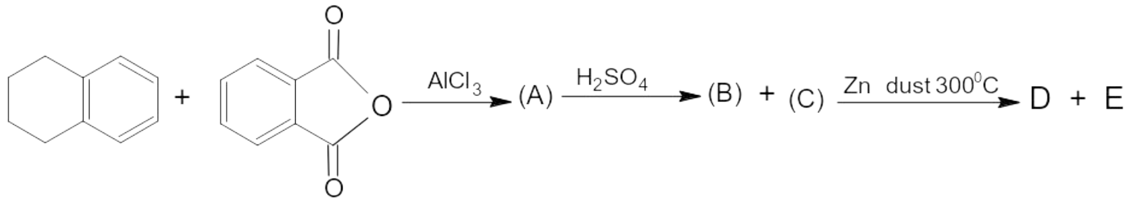


(III)

Which one is correct increasing order of ease of decarboxylation in acid

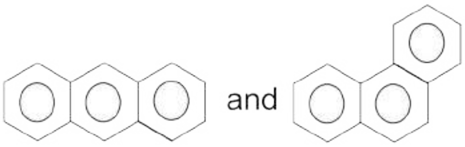
(a) II < I < III
(b) I < II < III
(c) II < I < II
(d) II < III < I

4.

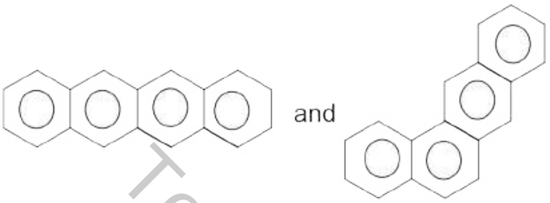


D and E are

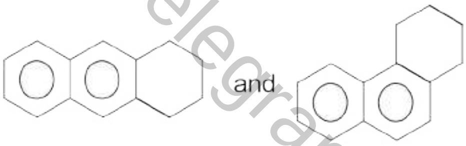
(a)



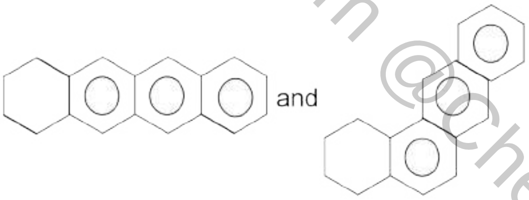
(b)



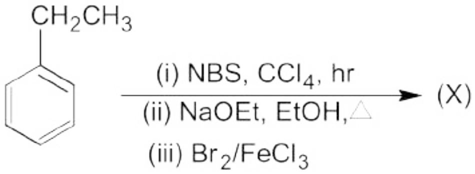
(c)



(d)

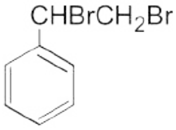


5. Which of the following compound is not formed.

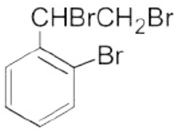


X represents mixture of organic compounds. The mixture does not contain.

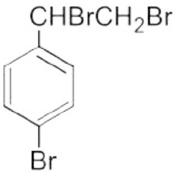
(a)



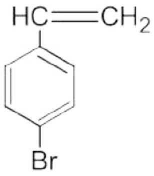
(b)



(c)

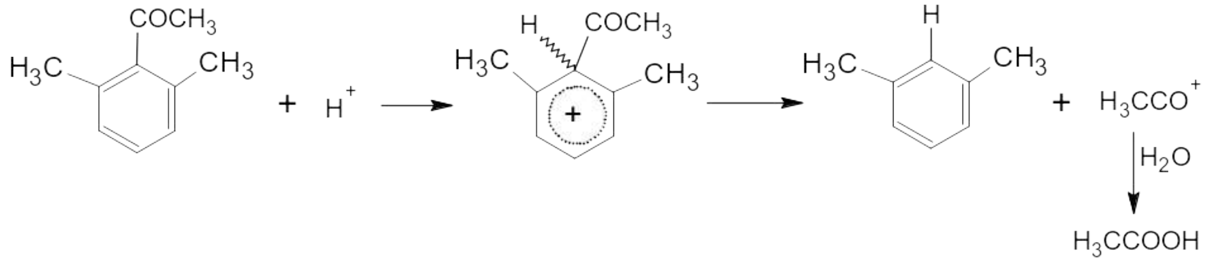


(d)



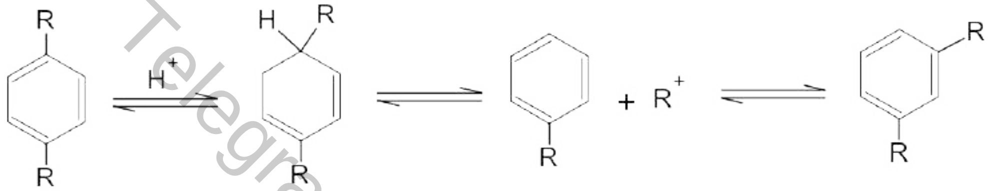
Solution :

1.

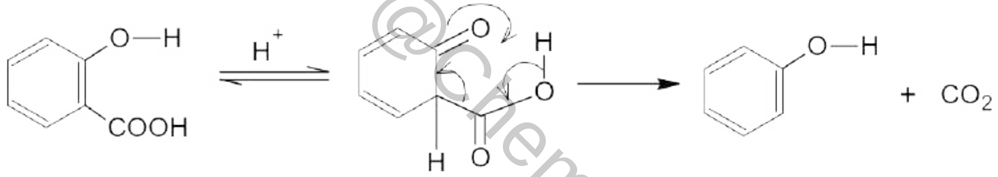


2. Rearrangement of alkyl groups, have been observed to produce symmetrical trisubstituted benzene when alkyl groups, larger than methyl are introduced. Under equilibrating condition, steric hindrance forces the system toward configuration having no two adjacent alkyl groups.

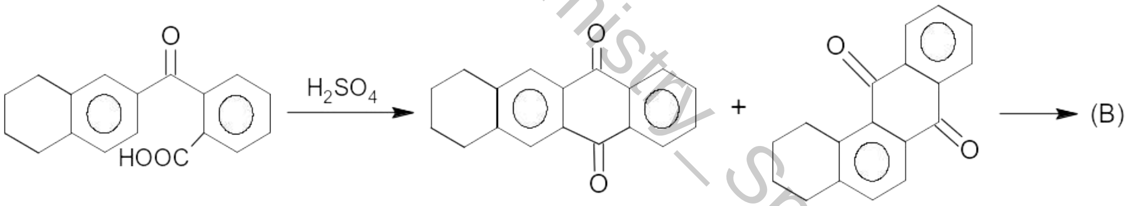
Dealkylation – realkylation



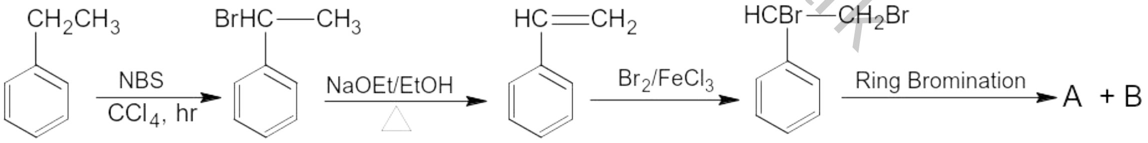
3. OH must be ortho or Para with ortho preferred.



4.



5.



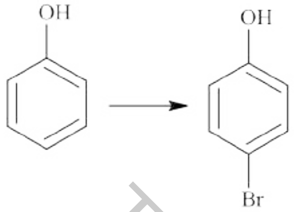
Write-up II

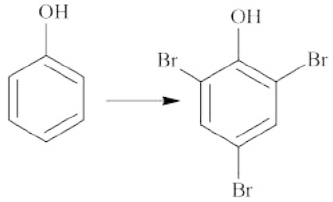
It is not always easy to predict the position of attack on multiply substituted benzene. If the benzene ring bears different ortho/para directing group at the 1 and 4 positions, the position of further substitution is not immediately clear. Sometimes steric effects determine the outcome. In other cases, electronic factors determine the outcome, and further reaction will be at the position activated by the more strongly activating group.

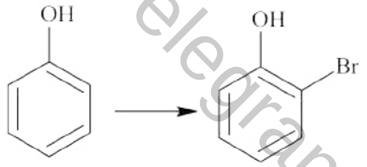
Some substituents are so strongly activating that no catalyst is needed, and it is often difficult to stop substitution after mono substitution. Mild conditions are needed to restrict the reaction to mono-substitution.

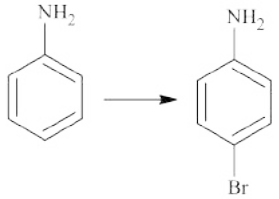
It is possible to reduce the activity such groups (by side chain reaction) so that the reaction can be stopped after mono substitution then and again by a side chain reaction the original group is restored. Effective use can sometimes be made of removable blocking groups on the ring.

1. Which of the following synthesis could not be done without involving blocking position on the ring?

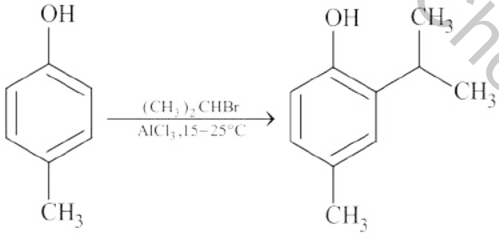
(a) 

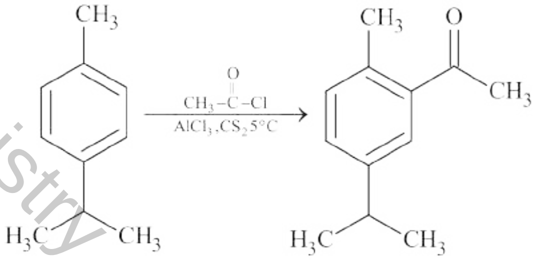
(b) 

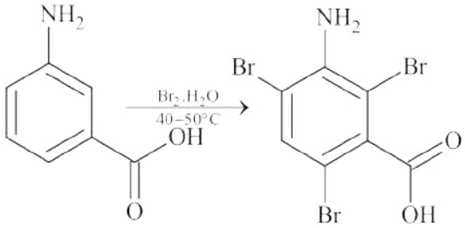
(c) 

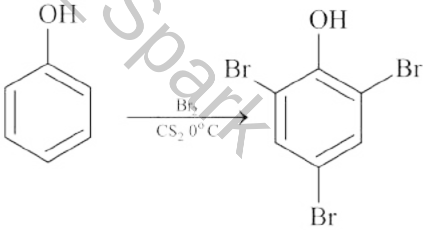
(d) 

2. Which of the following is not the correct major product?

(a) 

(b) 

(c) 

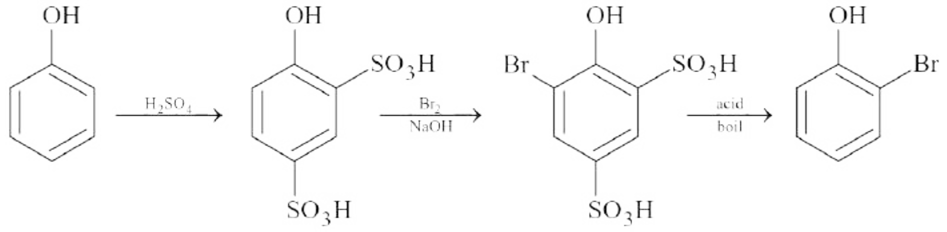
(d) 

3. Which of the following side chain reaction/s can be used to reduce the activity of strongly activating groups like —OH?

(a) Benzoylation
(b) Acetylation
(c) Both of the above
(d) None of the above

Solution :

1. **(c)** Ortho-bromo phenol can be prepared by protecting one O position and the p position by sulphonation



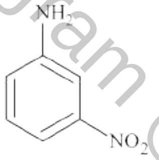
2. **(a)**

3. **(c)**

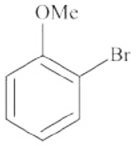
Subjective

Problem 1: Devise sequences for preparing the following compounds from benzene:

i)

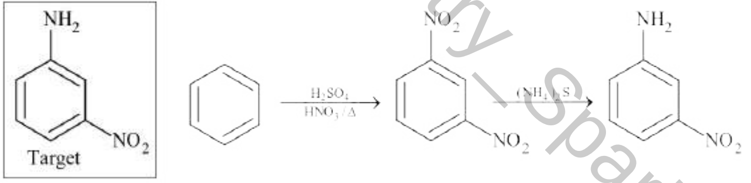


ii)

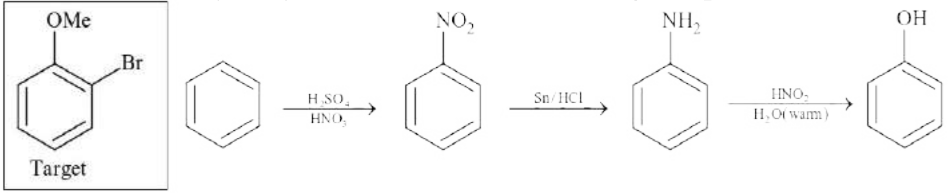


Solution:

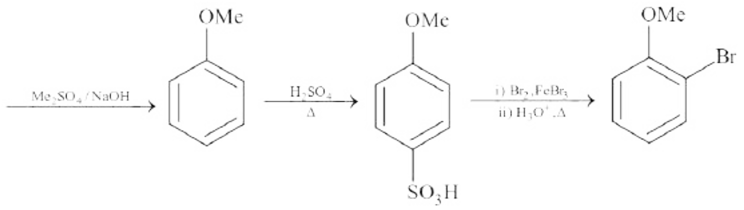
i) The process can be started if we can do the nitration to benzene ring two times and then can reduce one of the group selectively. Ammonium sulphide allows selective reduction of one nitro group in the presence of another. The mechanism of this reaction is complex. It is the transformation itself which you need to know.



ii) The target can be achieved if we can form phenol from benzene. Formation of phenol from benzene is not straight forward. The route shown below involves the nitration, reduction to the aniline and diazotization. "Hydrolysis" of the diazonium ion gives phenol.

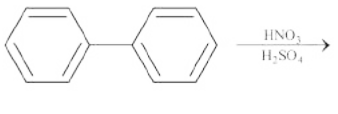


The next steps involve temporary introduction of a – SO_3 group as a protecting group of the para-position. This allows selective bromination of the ortho-position. (note: which products would you get without the –SO_3 group?)

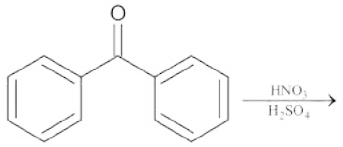


Problem 2: Show the exact structure of the product (or products) of each EAS reaction below. State whether each reaction is expected to be faster or slower than the corresponding reaction of benzene

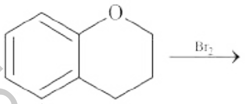
i)



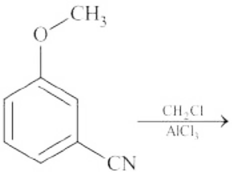
ii)



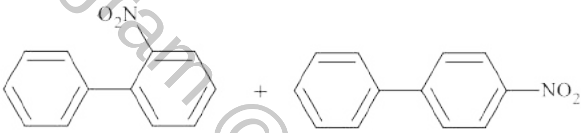
iii)



iv)

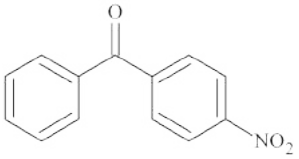


Solution: i)



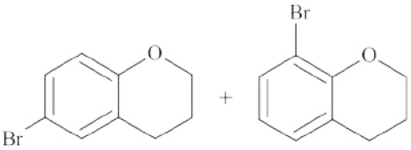
each phenyl group acts as an activating ortho/para director to the other (equivalent) ring. This reaction would be faster than the nitration of benzene.

ii)

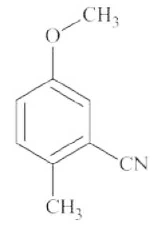


The carbonyl group acts as a deactivating meta director to both (equivalent) rings. This reaction will be slower than the nitration of benzene.

ii)

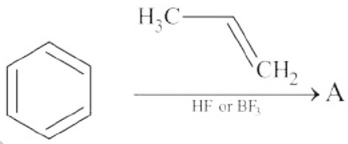


The oxygen – containing ring can be viewed as an OR group and an R group attached to the benzene ring. Although both groups are activating, the OR group is more strongly activating, so the position ortho and para to it will be brominated. This reaction will be faster than the bromination of benzene, which requires a catalyst.

iv) 

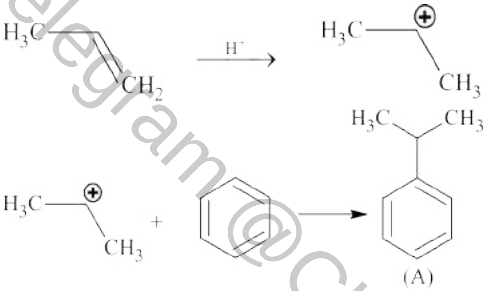
The reaction will be faster than that of benzene because of the activating nature of OCH_3 group which will be dominating over the deactivating group CN.

Problem 3:



Identify A and also the electrophile involved in the reaction.

Solution:



A is iso propyl benzene (cumene) and electrophile involved is $CH_3 - CH^{\oplus} - CH_3$ (Isopropyl carbocation). Rearrangements are also possible in Friedel Crafts, reactions when benzene is treated with n-butyl chloride and Lewis acid the product obtained is isobutyl benzene.

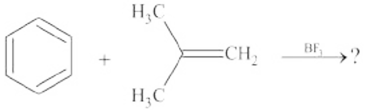
Problem 4: What happens when benzene is treated with methyl chloride in presence of anhydrous $AlCl_3$ and the product is treated with excess of chlorine in presence of UV light?

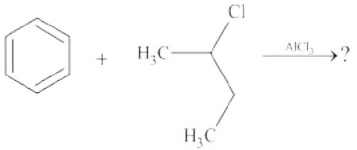
Solution:

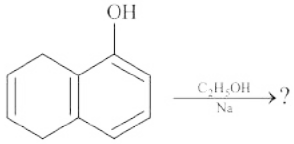
$$\underset{\text{Benzene}}{C_6H_6} + CH_3Cl \xrightarrow[AlCl_3]{\text{anhy.}} C_6H_5CH_3 \xrightarrow[\text{UV light}]{Cl_2} C_6H_5CH_2Cl \xrightarrow{Cl_2} C_6H_5CHCl_2$$

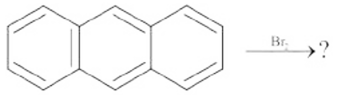
$$\xrightarrow{Cl_2} \underset{\text{Benzotrichloride}}{C_6H_5CCl_3}$$

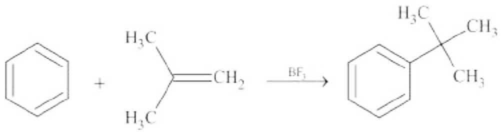
Problem 5: Complete the following

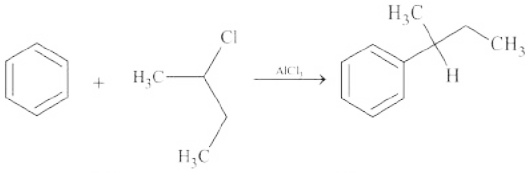
a) 

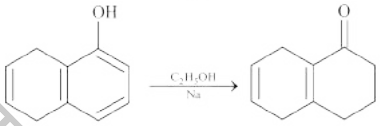
b) 

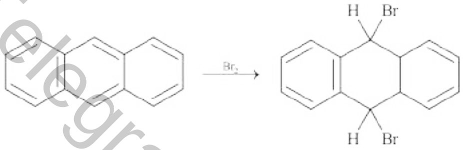
c) 

d) 

Solution: a) 

b) 

c) 

d) 

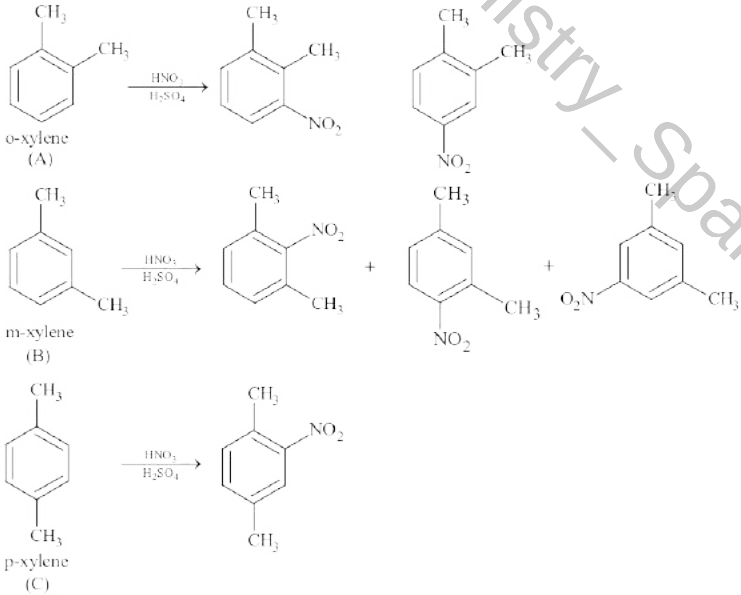
Problem 6: Compounds (A), (B) and (C) are three methyl isomeric derivatives of benzene. Identify which is o-, m- or p- from the products of nitration?

$A \xrightarrow[H_2SO_4]{\text{conc. } HNO_3}$ two mononitro product

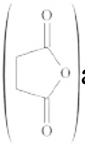
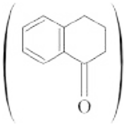
$B \xrightarrow[H_2SO_4]{\text{conc. } HNO_3}$ three mononitro products

$C \xrightarrow[H_2SO_4]{\text{conc. } HNO_3}$ one mononitro product

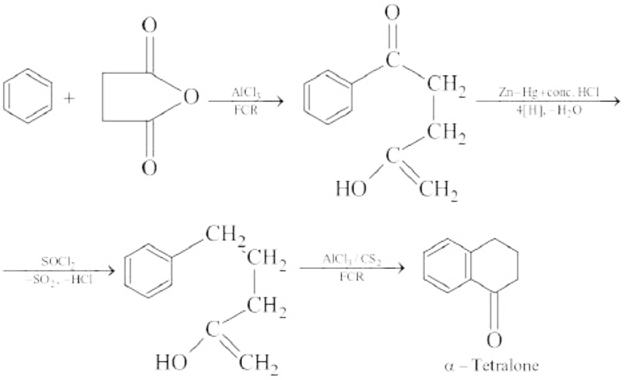
Solution:



Problem 7:

Starting with benzene and succinic  anhydride synthesise α -tetralone ().

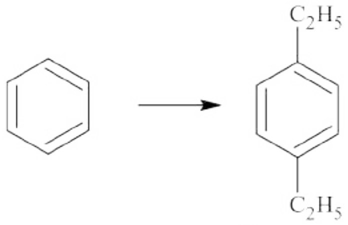
Solution:



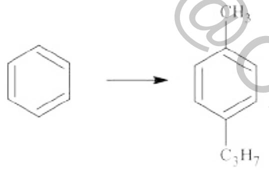
Problem 8: How the following conversions are achieved?

a) $C_6H_5C_2H_5 \longrightarrow C_6H_6$

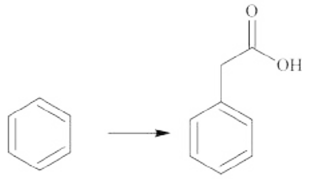
b)



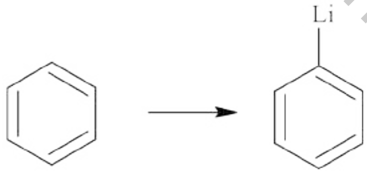
c)



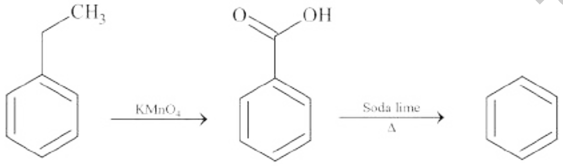
d)



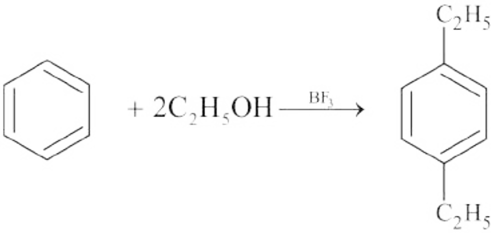
e)



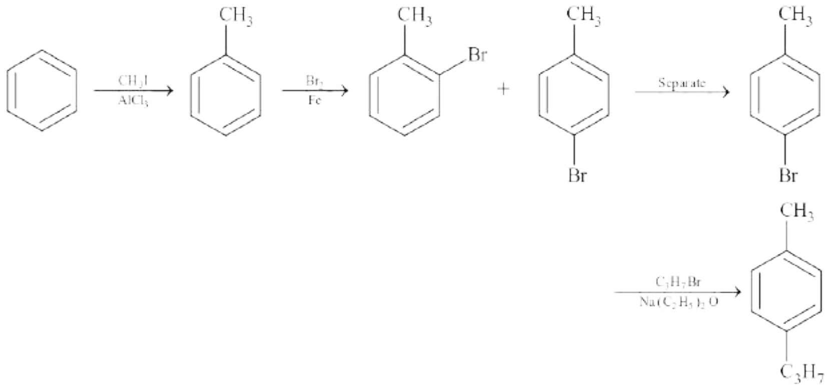
Solution: a)



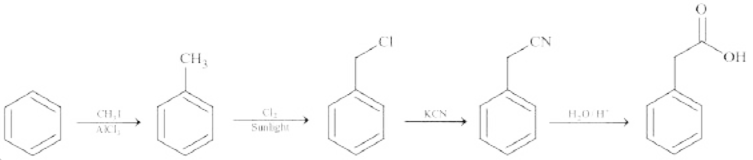
b)



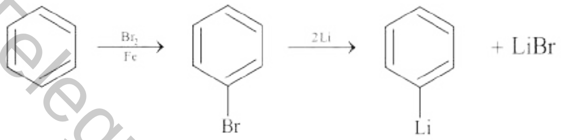
c)



d)

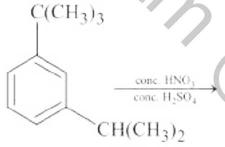


e)



Problem 9: Predict the major monosubstituted product in the following cases.

a)



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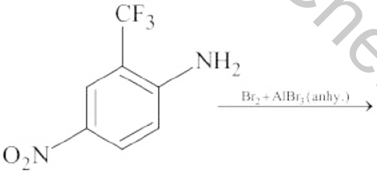
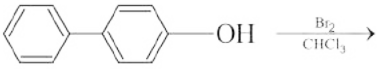
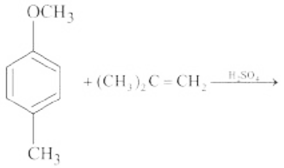


c)

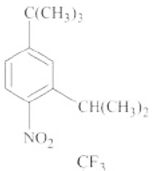


d)



Solution:

a)



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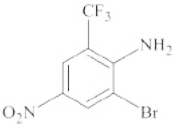

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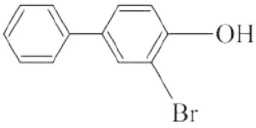

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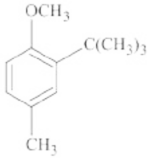
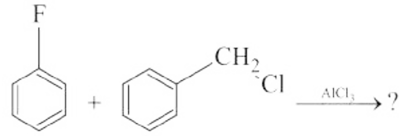
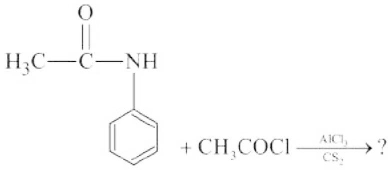


Problem 10: Write the structure of the major product (only monosubstitution is involved in each case)

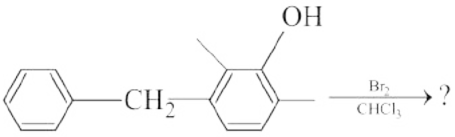
i)



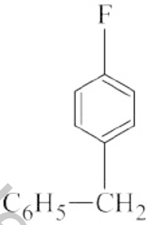
ii)



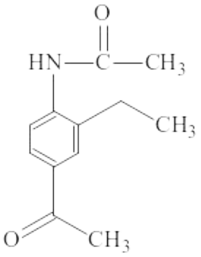
iii)



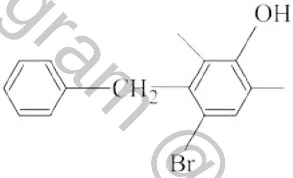
Solution: i)



ii)



iii)

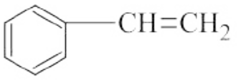


Problem 11: Hydrocarbon (A) with molecular formula C_8H_8 gave the following reactions:

1. On shaking with bromine, a bromo derivative (B) $C_8H_8Br_2$ was formed.
2. Vigorous oxidation of the hydrocarbon with alkaline $KMnO_4$ gave a monobasic acid (C).
3. Acid (C) on distillation with sodalime gave C_6H_6. Deduce structures of A, B and C and name compound (A).

Solution:

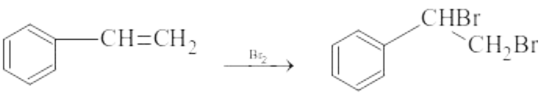
1. The molecular formula of (A) and step (3) suggest (A) to be an aromatic organic compound.
2. Step (2) suggests that (A) has a double bond in side chain. Thus, (A) may be



(A) Phenylethene or Vinylbenzene or Styrene

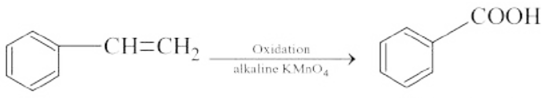
Reaction:

1.



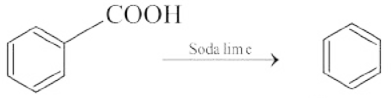
(B)

2.



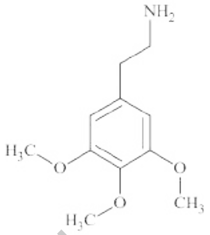
(C)Benzoic acid

3.



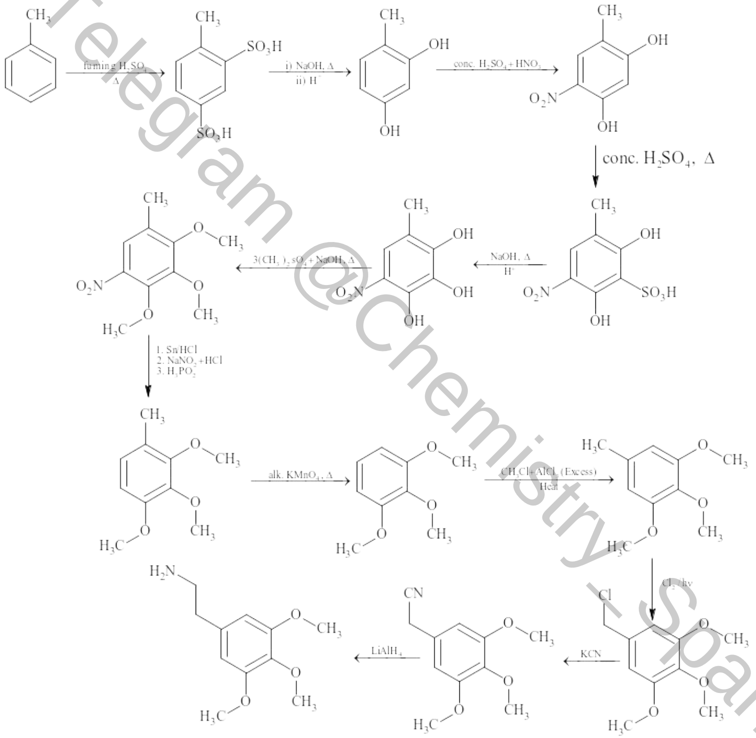
benzene

Problem 12: Describe how mescaline could be synthesized from toluene



mescaline

Solution

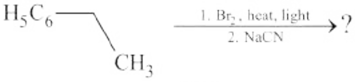


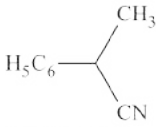
Assignments (New Pattern)

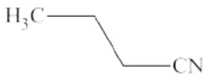
SECTION – I Single Choice Questions

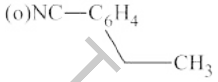
Level - I

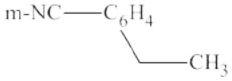
1. Write the major product of the following reaction:



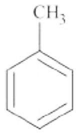
(a) 

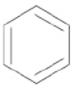
(b) 

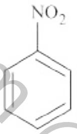
(c) 

(d) 

2. Among the following compounds (I – III), the correct order in reaction with electrophile is

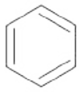

I

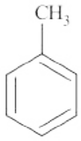

II


III

(a) II > III > I
(b) III > I > II
(c) I > II > III
(d) I = II > III

3. Identify the correct order of reactivity in electrophilic substitution reactions of the following compounds:


1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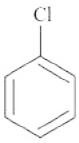
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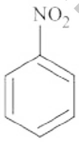
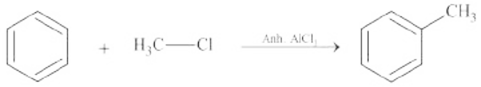
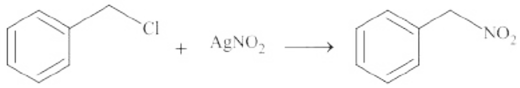
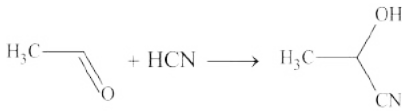

4

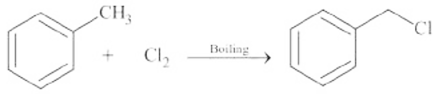
(a) 1 > 2 > 3 > 4
(b 4 > 3 > 2 > 1
(c) 2 > 1 >3 > 4
(d) 2 > 3 > 1 > 4

4. Which one of the following is a free radical substitution reaction?

(a) 

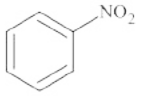
(b) 

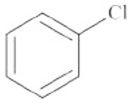
(c) 

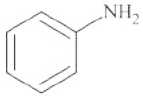
(d) 

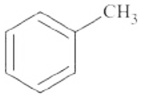
5. The treatment of benzene with isobutene in the presence of sulphuric acid gives
(a) isobutyl benzene (b) tert-butyl benzene
(b) n-Butyl benzene (d) No reaction

6. Which of the following compounds will be most easily attacked by an electrophile?

(a)


(b)


(c)


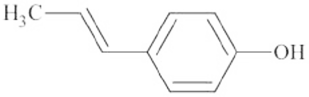
(d)


7. In Friedel Craft's alkylation, besides $AlCl_3$, the other reactants are
(a) $C_6H_6 + NH_2$ (b) $C_6H_6 + CH_4$
(c) $C_6H_6 + CH_3Cl$ (d) $C_6H_6 + CH_3COCl$

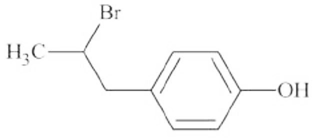
8. The reaction,
Benzene + Methy halide $\xrightarrow{\text{anhyd. AlCl}_3}$ toluene, is known as
(a) Kolbe reaction (b) Wurtz reaction
(c) Perkin reaction (d) Friedel-Crafts reaction

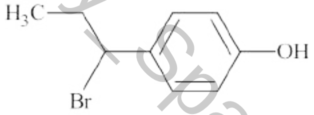
9. The correct order of C – C bond lengths in benzene (I), ethane (II), ethylene (III) and acetylene (IV) is
(a) II > III > IV > I (b) IV > III > II > I
(c) II > I > III > IV (d) IV > III > I > II

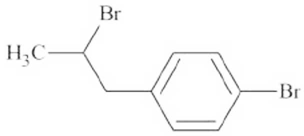
10. The reaction of



with HBr gives

(a)


(b)


(c)


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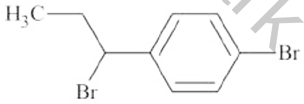
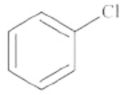


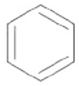
(c) I > II > III > IV (d) II > I > III > IV

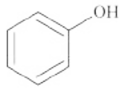
11. A group which deactivates the benzene ring towards electrophilic substitution but directs the incoming group towards o- and p- positions is
(a) $-NH_2$ (b) $-Cl$
(c) $-NO_2$ (d) $-C_2H_6$

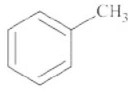
12. The most reactive compound for electrophilic nitration is
(a) Benzene (b) Nitrobenzene
(c) Benzoic acid (d) Toluene

13. Which one of the following compounds will be most easily attacked by an electrophile?

(a) 

(b) 

(c) 

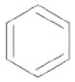
(d) 

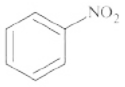
14. Benzene reacts with CH_3COCl in presence of Lewis acid gives

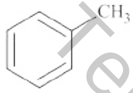
(a) Chlorobenzene (b) Toluene

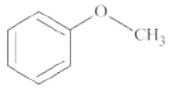
(c) Benzyl chloride (d) Acetophenone

15. Which of the following will have fastest rate of reaction with $Br_2/FeBr_3$

(a) 

(b) 

(c) 

(d) 

Level - II

1. The ortho/para directing group among the following is

(a) –COOH (b) –CN

(c) $–COCH_3$ (d) $–NHCOCH_3$

2. Benzoic acid, when heated with soda lime yields

(a) benzaldehyde (b) benzene

(c) toluene (d) benzylalcohol

3. In the Friedel-Crafts synthesis of toluene, reactants in addition to anhydrous $AlCl_3$ are

(a) $C_6H_6 + CH_4$ (b) $C_6H_6 + CH_3Cl$

(c) $C_6H_5Cl + CH_3Cl$ (d) $C_6H_5Cl + CH_4$

4. Benzene does not undergo addition reactions easily because

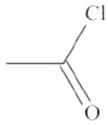
(a) It has a cyclic structure

(b) Double bonds in it are very strong

(c) Resonance stabilized system is to be preserved

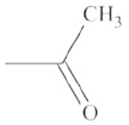
(d) It has six hydrogen atoms

5. Which of the following groups is *ortho* and *para* directing?

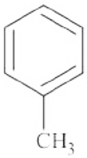
(a) 

(b) — CHO

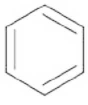
(c) — OH

(d) 

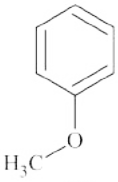
6. Among the following compounds, the decreasing order of reactivity towards electrophilic substitution is



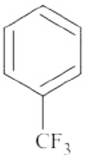
I



II



III



IV

(a) III > I > II > IV (b) IV > I > II > III
(c) II > I > IV > III (d) III > I > II > IV

7. Which species represents the electrophile in aromatic nitration?
(a) NO_2^- (b) NO_2^+
(c) NO_2 (d) NO_3^-

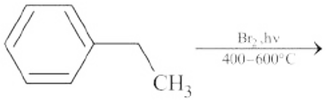
8. The function of $AlCl_3$ in Friedel Crafts reaction is
(a) to absorb water (b) to absorb HCl
(c) to produce electrophile (d) to produce nucleophile

9. What is the end product obtained by nitration of toluene?
(a) o-Nitrotoluene (b) p-Nitrotoluene
(c) 2,4-Dinitrotoluene (d) 2,4,6-Trinitrotoluene

10. Ozonolysis of p-xylene gives
(a) Glyoxal (b) Methyl glyoxal
(c) Both of these (d) None of these

SECTION – II **May be more than one choice**

1. The major products of the following bromination reaction



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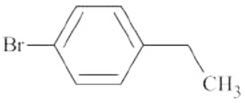

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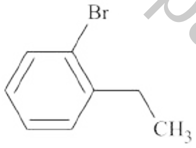

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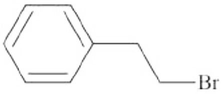

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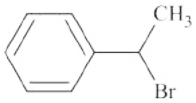
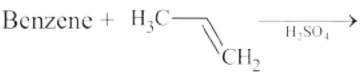


2. Isopropylbenzene can be prepared by

(a)


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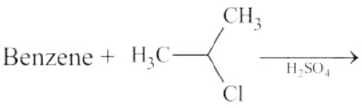

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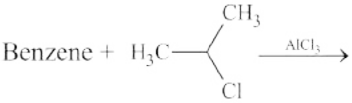

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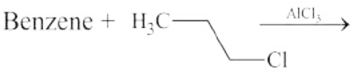
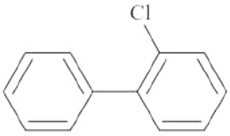
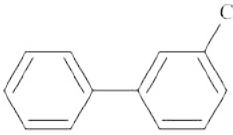
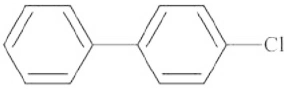
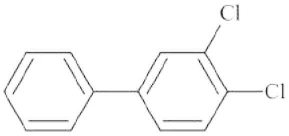


3. The reaction of biphenyl with HOCl in the presence of a strong acid gives

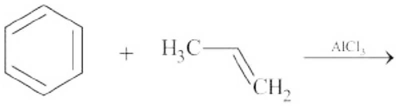
(a) 

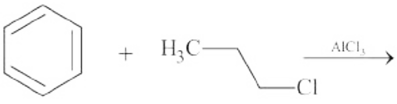
(b) 

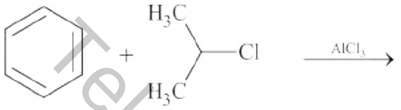
(c) 

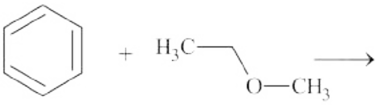
(d) 

4. Isopropylbenzene can be obtained by

(a) 

(b) 

(c) 

(d) 

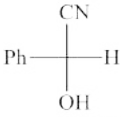
5. Which of the following groups are ortho and para-directing?
(a) – OH
(b) – CHO
(c) – CN
(d) – $NHCOCH_3$

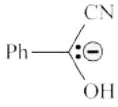
6. m-Nitrobenzoic acid can be obtained by
(a) toluene $\xrightarrow[KMnO_4]{[O]}$ A $\xrightarrow[H_2SO_4]{HNO_3}$
(b) toluene $\xrightarrow[CrOCl_2]{[O]}$ A $\xrightarrow[H_2SO_4]{HNO_3}$ B $\xrightarrow[KMnO_4]{[O]}$
(c) toluene $\xrightarrow[HNO_3+H_2SO_4]{\text{nitration}}$ A $\xrightarrow[KMnO_4]{[O]}$
(d) all these methods

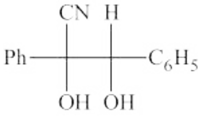
7. The necessary conditions for halogenation of benzene are
(a) low temperature
(b) darkness
(c) the presence of a halogen carrier
(d) I_2 + conc. HNO_3

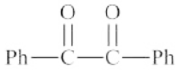
8. Benzene can undergo
(a) substitution
(b) addition
(c) elimination
(d) oxidation

9. Which of the following intermediate stages are possible in the conversion of benzaldehyde into benzoin by reaction with HCN?

(a) 

(b) 

(c) 

(d) 

10. Iodobenzene can be obtained by

(a) $C_6H_6 + I_2 \longrightarrow$ (b) $C_6H_6 + I_2 \xrightarrow{HNO_3}$

(c) $C_6H_5N_2^+Cl^- + KI \longrightarrow$ (d) $C_6H_6 + HI \longrightarrow$

11. Toluene, when treated with Br_2/Fe, gives p-bromotoluene as the major product because the $-CH_3$ group

(a) is ortho - para directing (b) is meta directing

(c) activates of the ring by hyperconjugation (d) deactivates the ring

SECTION – III

Other Engg. Exams question

1. The end product of the reaction,

$C_6H_6 \quad + \quad Cl_2 \xrightarrow{Sunlight}$ is :

(a) C_6H_5Cl (b) o-$C_6H_4Cl_2$

(c) $C_6H_6Cl_6$ (d) p-$C_6H_4Cl_2$

[PMT (MP) 1993 ; Roorkee 1999]

2. Which of the following is explosive ?

(a) Nitrobenzene (b) Nitrophenol

(c) Nitromethane (d) Trinitrobenzene

[PMT (MP) 1993]

3. The reaction,

$C_6H_6 \quad CH_3Cl \xrightarrow[AlCl_3]{Anhydous} C_6H_5CH_3 \quad + \quad HCl$

is an example of :

(a) Friedel-Crafts reaction (b) Kolbe's synthesis

(c) Wurtz reaction (d) Grignard synthesis

[CPMT 1990]

4. Which of the following alcohols is dehydrated most readily with conc. H_2SO_4?

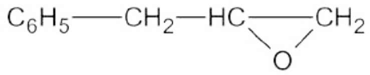
(a) p-$O_2NC_6H_4CH(OH)CH_3$ (b) p-$ClC_6H_4CH(OH)\ CH_3$

(c) p-$CH_3OC_6H_4CH(OH)CH_3$ (d) $C_6H_5CH(OH)\ CH_3$

5. The major product obtained when 3-phenyl-1, 2-propane-diol is heated with H_2SO_4 is :

(a) $C_6H_5 - CH_2 - CO - CH_3$ (b) $C_6H_5 - CH_2 - CH_2 - CHO$

(c) $C_6H_5 - CH_2 - CH = CH_2$

(d)


6. The correct sequence of activating power of a group in benzene is:

(a) $-NH_2 >$ - $NHCOCH_3 >$ -CH_3 (b) $-NH_2 <$ -$NHCOCH_3 <$ - CH_3

(c) $-NH_2 >$ -$NHCOCH_3 <$ -CH_3 (d) $-$ $NH_2 <$ - $NHCOCH_3 >$ -CH_3

7. Phenol is :

(a) A base weaker than NH_3

(b) An acid stronger than carbonic acid

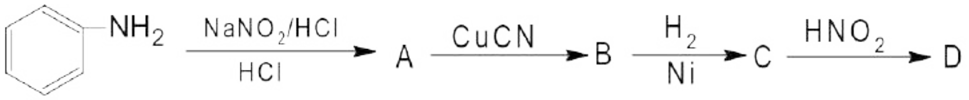
(c) An acid weaker than carbonic acid
(d) Neutral

[PMT (MP) 1990]

8. Between p-nitrophenol and salicylaldehde, solubility in base is :
(a) Almost nil in both cases
(b) Higher in p-nitrophenol
(c) Higher for salcylaldehyde
(d) Equal in nature

[CBSE (PMT) 1991]

9. Aniline in a set of reactions yielded a product D

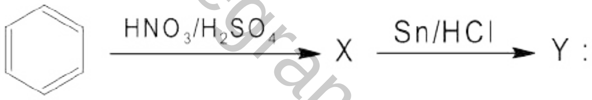


The structure of the product D would be:

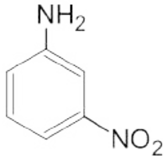
(a) $C_6H_5NHCH_2CH_3$
(b) $C_6H_5CH_2OH$
(c) $C_6H_5CH_2NH_2$
(d) C_6H_5NHOH

[CBSE (PMT) 2005]

10. Identify Y in the change;



(a)



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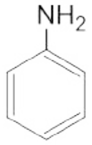

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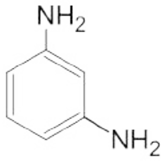

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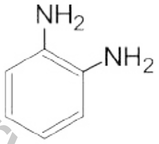


[AMU (Aligarh) 1992]

11. Benzyl chloride is formed by treating toluene with Cl_2 in :
(a) Presence of light
(b) Absence of light
(c) Treating benzene with anhy. $AlCl_3$.
(d) Treating benzene with As_2S_3

[CPMT 1991]

12. Benzene is converted to toluene by :
(a) Friedel-Crafts reaction
(b) Grignard reaction
(c) Wurtz reaction
(d) Perkin reaction

[CET (Karnataka) 1993]

13. Increasing order of acid strength among p-methoxypenol, p-methylphenol and p-nitrophenol is :
(a) p-methylphenol < p-methoxyphenol < p-nitrophenol
(b) p-methoxyphenol < p-methylphenol < p-nitrophenol
(c) p-nitrophenol < p-methoxyphenol < p-methylphenol
(d) p-nitrophenol < p-methylphenol < p-methoxyphenol

[CBSE (PMT) 1993]

14. Aniline is reacted with bromine water and the resulting product is treated with an aqueous solution of sodium nitrite in the presence of dilute HCl. The compound so formed is treated with fluoroboric acid which is subsequently heated dry. The final product is
(a) p-bromofluorobenzene (b) p-bromoaniline
(c) 2, 4, 6-tribromofluorobenzene (d) 1, 3, 5-tribromobenzene
[CBSE (PMT) 1998]

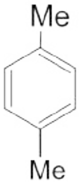
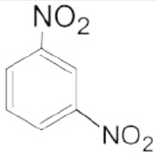
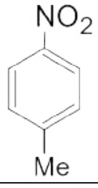
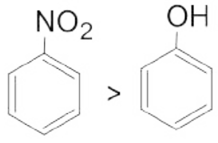
15. Nitrobenzene can be prepared from benzene by using a mixture of conc. HNO_3 and conc. H_2SO_4. In the nitrating mixture HNO_3 acts as a:
(a) Base (b) acid
(c) Reducing agent (d) catalyst
[AIMS 1998]

SECTION – IV **Match the column**

1. Match the following

Column – I	Column – II
(a) Cyclic conjugated polyenes with $(4n + 2)\pi$-electrons	(p) Arenes and alkyl halides in presence of anhydrous $AlCl_3$
(b) o-dichlorobenzene does not exist as two isomers	(q) Aromatic compounds
(c) Friedel crafts reaction	(r) Delocalization of π-electrons
(d) Meta directing group	(s) Deactivates the ring towards electrophilic substitution

2. Match the column

Column – I	Column – II
(a) 	(p) meta position is more deactivated
(b) 	(q) ortho with respect to methyl group
(c) 	(r) only one mono substituted product
(d) 	(s) meta with respect to NO_2

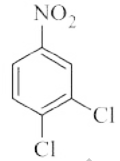
SECTION – V Comprehension Type Questions

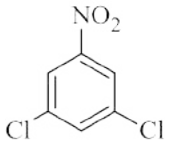
Write-up I

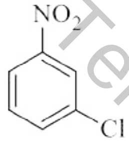
A third group is least likely to enter between two groups in the meta relationship. This is the result of steric hindrance and increases in importance with the size of the groups on the ring and with the size of the attacking species.

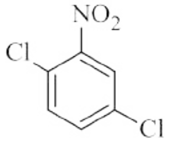
When a Meta-directing group is meta to an ortho-para directing group, the incoming group primarily goes ortho to the meta directing group rather than para.

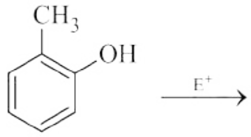
1. Chlorination of m-chloro nitro benzene gives

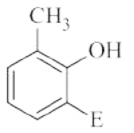
(a) 

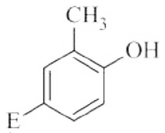
(b) 

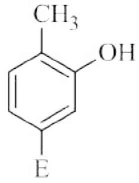
(c) 

(d) 

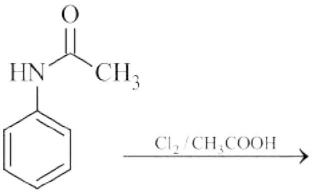
2. 

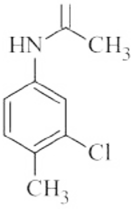
(a) 

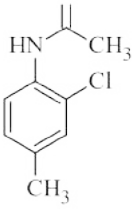
(b) 

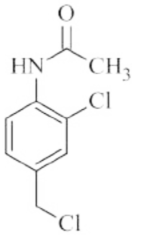
(c) 

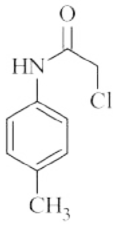
(d) (a), (b)

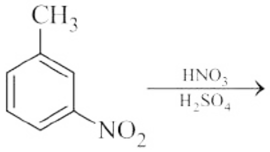
3. 

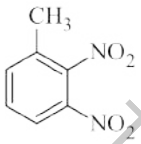
(a) 

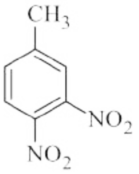
(b) 

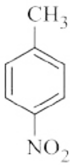
(c) 

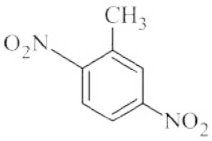
(d) 

4. 

(a) 

(b) 

(c) 

(d) 

✍ **Write-up II**

The leaving group is the functional group that is eliminated with electrons of the σ-bond in a reaction. The nature of the leaving group is important to both S_N1 and S_N2 reactions. Better the leaving group faster is the reaction. The relative leaving ability of leaving group Y in R – Y is enhanced by.

i) the strength of the R – Y bond
ii) the polarizability of R – Y bond
iii) the stability of Y^- and
iv) the degree of stabilization through solvation of Y.

5. Which one of the following is good leaving group?

(a) Triflate
(b) Mesylate
(c) Tosylate
(d) all are equal

6. Which one of the following statement is correct?

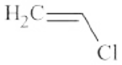
(a) The nature of leaving group important to S_N1 only
(b) The nature of leaving group important to S_N2 only
(c) The nature of leaving group important to S_N1 and S_N2
(d) All

7. Which one of the following is correct statement?

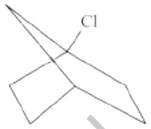
(a) HO^-, RO^- and NH_2^- are strong bases and therefore are good leaving groups
(b) I^- is good leaving group than F^-
(c) charged species are bad leaving groups than neutral leaving groups
(d) The conjugate bases of strong oxygen acids such as Tosylate are bad leaving group

8. Which one of the following is correct?
   (a) Protonation of alcohols with strong acids converts the poor leaving group hydroxyl group into much better leaving group.
   (b) The hydroxyl group converted into a good leaving group by reaction of alcohols with p-toluensulfonxyl chloride
   (c) the amine group converted into a good leaving group by treated with HNO_2 5°C in primary amines
   (d) RO^- is strong base therefore good leaving group.

9. Which is/are not readily under goes nucleophilic substitution?

(a) 

(b) Ph—Cl

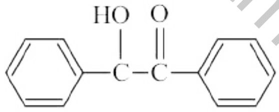
(c) 

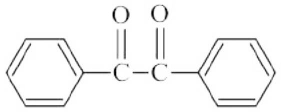
(d) All of these

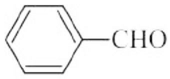
Write-up III

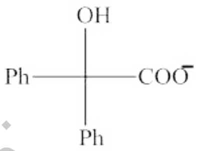
$$C_6H_6 + CH_3Cl \xrightarrow[AlCl_3]{Anhy} A \xrightarrow{SeO_2} B \xrightarrow[alcoholic]{CN^-} C \xrightarrow{Dil.\ HNO_3} D \xrightarrow{Dil.\ OH^-} E$$

10. In the above reaction 'E' is

(a) 

(b) 

(c) 

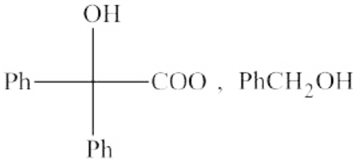
(d) 

$$Ph-\overset{OH}{\underset{Ph}{C}}-COO^-$$

11. The order of reaction from 'B' to C
    (a) I
    (b) II
    (c) III
    (d) zero

12. Para nitro benzaldehyde undergo
    (a) benzoin condensation
    (b) Aldol condensation
    (c) Cannizaro reaction
    (d) None of these

13. Benzaldehyde in presence of conc. NaOH produces
    (a) $PhCOO^-$, $PhCH_2OH$
    (b) Ph–CO–CO–Ph, Ph–CHOH–CO–Ph

(c) 

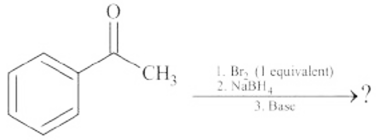
$$Ph-\overset{OH}{\underset{Ph}{C}}-COO,\ PhCH_2OH$$

(d) $PhCOO^-$, Ph–CO–CO–Ph

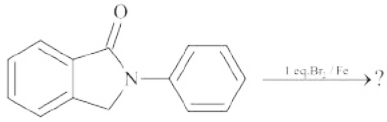
SECTION – VI Subjective Questions

LEVEL – I

1. Predict the major product in each of the following reactions.



2. What would be the major product in following reaction?

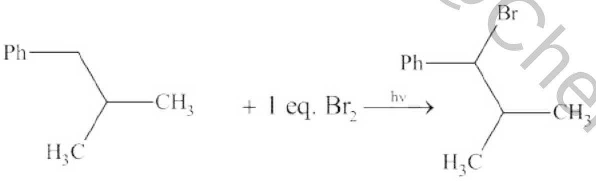


3. When benzene is treated with DCl at low temperatures a compound C_6H_6DCl©, is formed. On warming the reactants, C_6H_6 and DCl are re-formed. However, in the presence of $AlCl_3$ an isomer of C_6H_6DCl(D) is produced, which on warming, gives mainly C_6H_5D and HCl. Explain

4. Give structure of the principal organic products expected from mononitration of

a) o-nitrotoluene b) m-dinitrobenzene
c) m-cresol d) m-nitrotoluene

5. Account of the following

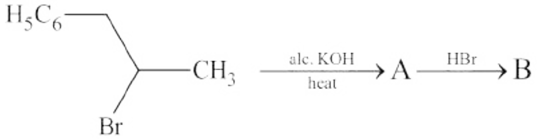


with little or no $PhCH_2C(Br)(CH_3)_2$ formed.

6. C_7H_7Cl has four isomers A_1, A_2, A_3 and A_4

$A_4 \xrightarrow[\text{II) Soda lime, }\Delta]{\text{I) KMnO}_4}$ Benzene, Identify A_1, A_2, A_3 and A_4.

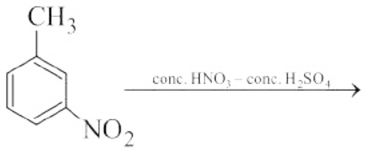
7.



8. Oxidation of toluene by acidic $KMnO_4$ gives poor yield of benzoic acid while oxidation of p-nitrotoluene gives good yield of p-nitrobenzoic acid. Why?

9. What happens when p-xylene is treated with concentrated sulphuric acid and the resultant product is fused with KOH?

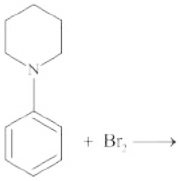
10.

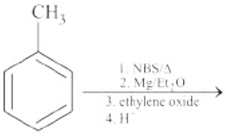


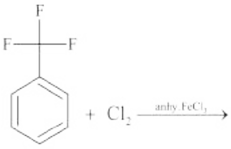
In the above reaction which product is most likely to be formed?

LEVEL – II

1. Give the products of the following reactions

a)


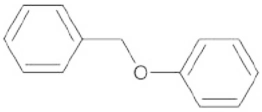
b)


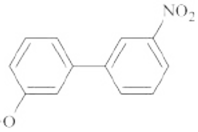
c)


2. An aromatic compound A ($C_7H_7NO_2$) on reduction gives B (C_7H_9N). Diazotization of B and subsequent treatment with CuCN/KCN gives C ($C_8H_8O_2$). Hydrolysis of C followed by oxidation forms D, which has equivalent mass of 83g eq^{-1}. D forms only one mono substitution product. Give structure for A, B, C and D.

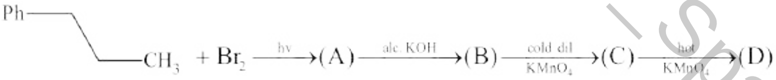
3. A compound ($C_8H_{10}O$) upon treatment with alkaline solution iodine gives a yellow precipitate. The filtrate on acidification gives a white solid E ($C_7H_6O_2$). Write the structures of D, E and explain the formation of E.

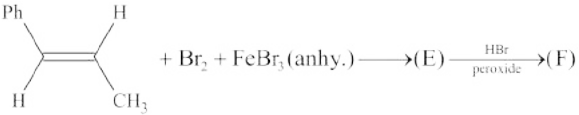
4. Give the product(s) obtained from the reaction each of the following compounds with $Br_2/FeCl_3$.

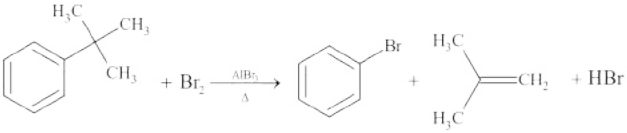
a)


b)


5. Write the structures of the compounds from the following data.

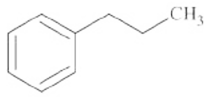
a)


b)


6.


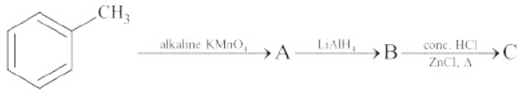
7. Compounds (A) and (B) are isomers having the formula C_8H_{10}. On oxidation (A) gives benzoic acid while (B) gives phthalic acid which forms an anhydride (C) on heating. Identify (A), (B) and (C).

8. How will you synthesize



from benzene?

9. Identify A to C in the following:



10. Complete the following reactions:
    a) 4-bromo-2-methylphenol treated with 2-methylpropene and sulphuric acid.
    b) p-cresol treated with propanoyl chloride and aluminium chloride.
    c) 2,5-dichlorophenol reacts with chlorine in acetic acid.

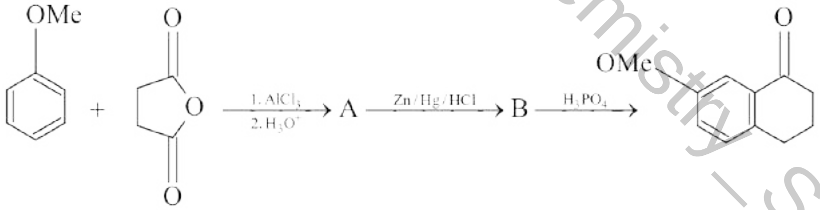
LEVEL – III (Judge yourself at JEE level)

1. Phenyl ring is known to exert negative inductive effect. But each phenyl ring in biphenyl $(C_6H_5 - C_6H_5)$ is more reactive than benzene towards electrophilic substitution. Explain.

2. Show synthesis of p-bromonitrobenzene from benzene in two steps.

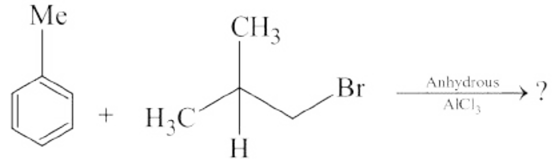
3. Fill in the blanks with appropriate structure of reaction products in the following transformations:
$o - HOOC - C_6H_4 - CH_2 - C_6H_5 \xrightarrow{SOCl_2} A \xrightarrow[AlCl_3]{Anhydrous} B \xrightarrow[HCl]{Zn-Hg} C$ **[IIT-1995]**

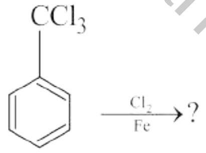
4. Predict the structures of the intermediates/products in the following reaction sequence.



[IIT-1996]

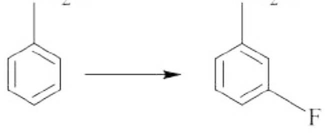
5. Predict the product

i)


ii)


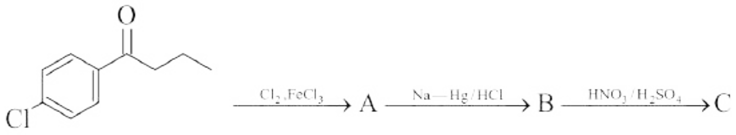
[IIT 1997]

6. Convert



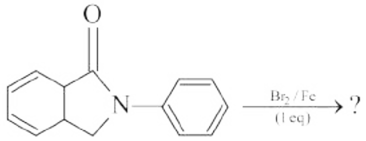
[IIT-2003]

7. Predict the product



[IIT-2002]

8. Predict the product



[IIT-2000]

9. 7-bromo-1, 3, 5-cycloheptatriene exists as a ionic substance whereas 5-bromo-1, 3-cyclopentadiene does not ionize even in the presence of Ag^+ ion. Explain? **[IIT-2004]**

Answers to Assignments

SECTION - I

Level - I

1.	**(a)**	4.	**(d)**	7.	**(c)**	10.	**(b)**	13.	**(c)**
2.	**(c)**	5.	**(b)**	8.	**(d)**	11.	**(b)**	14.	**(d)**
3.	**(c)**	6.	**(c)**	9.	**(c)**	12.	**(d)**	15.	**(d)**

Level - II

1.	**(d)**	3.	**(b)**	5.	**(c)**	7.	**(b)**	9.	**(c)**
2.	**(b)**	4.	**(c)**	6.	**(d)**	8.	**(c)**	10.	**(c)**

SECTION - II

1.	**(a), (c),(d)**	5.	**(a), (d)**	9.	**(a), (b), (c)**
2.	**(a), (b), (c), (d)**	6.	**(a), (b)**	10.	**(b), (c)**
3.	**(a) , (b), (c)**	7.	**(c), (d)**	11.	**(a, c)**
4.	**(a), (b), (c)**	8.	**(a), (b),(d)**		

SECTION – III Other Engg Exams.

1.	**(c)**	**2.**	**(d)**	**3.**	**(a)**	**4.**	**(c)**
5.	**(d)**	**6.**	**(a)**	**7.**	**(c)**	**8.**	**(b)**
9.	**(b)**	**10.**	**(b)**	**11.**	**(a)**	**12.**	**(a)**
13.	**(b)**	**14.**	**(c)**	**15.**	**(a)**		

SECTION – IV

1. **(a – q), (b – r), (c – p), (d – s)**

2. **(a – q, r), (b – r, s) , (c – q, r, s), (d – p)**

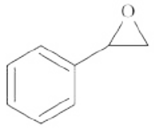
SECTION – V

1.	**(d)**	2.	**(d)**	3.	**(b)**	4.	**(d)**
5.	**(a)**	6.	**(c)**	7.	**(b)**	8.	**(b)**
9.	**(d)**	14.	**(d)**	15.	**(c)**		
16.	**(d)**						

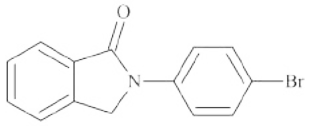
SECTION - IV

LEVEL - I

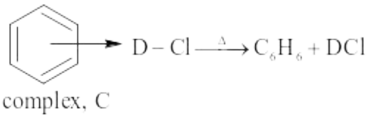
1.



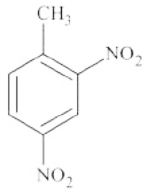
2.



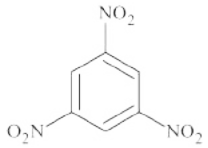
3. Since D is not incorporated into the benzene ring in the absence of $AlCl_3$, isomer C has no C – D σ bond. Instead, the D end of DCl is attracted to the π cloud of benzene to form a loosely bound π complex, indicated by an arrow in the structural formula. π complexes are also called charge – transfer complexes, because the electron – rich benzene ring, the donor molecule, transfers some electron density to the electron-poor D of DCl, acceptor molecule. With the catalyst $AlCl_3$, exchange of D^+ for H^+ occurs on warming. This exchange requires the formation of a C – D bond to give the σ complex. with D^+. The benzene ring is reformed by losing an H rather than the D because the C – H bond is weaker than the C – D bond. Notice the delocalization of the positive charge in the σ bond.



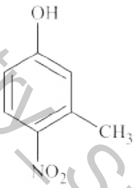
4. a)



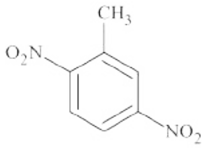
b)



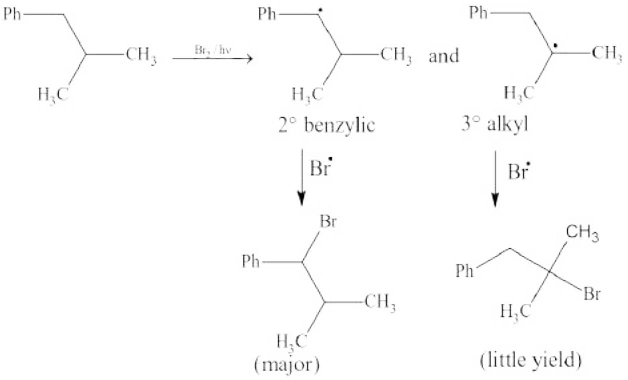
c)



d)



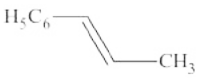
5.



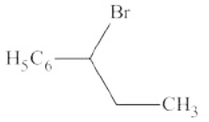
This reaction proceeds via free radical mechanism forming 2 free radicals, of which 2° benzylic free radical is stabilized more by resonance of phenyl ring and with hyperconjugation of $-CH_3$ group, thus resulting in the formation of $PhCH(Br)CH(CH_3)_2$ as the major product.

6. A_1, A_2, A_3 are o, p, m-chlorotoluenes A_4 - benzyl chloride

7. A =

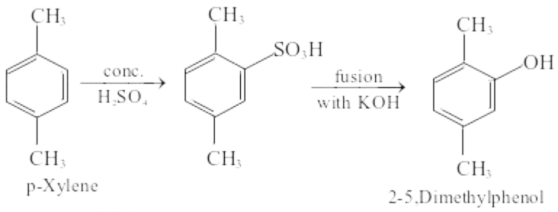


B =

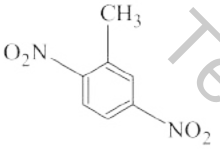


8. Oxidant is an electrophile, it can attack and destroy the ring in case of toluene. But in p-nitrotoluene, the $–NO_2$ group deactivates the electrophilic attack on benzene nucleus and thus increases the yield of p-nitrobenzoic acid.

9.

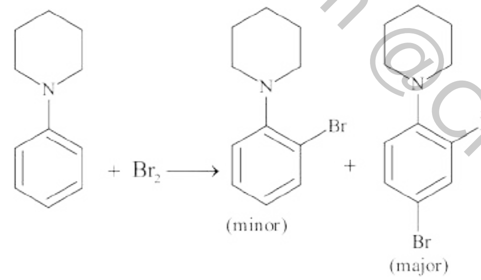


10.

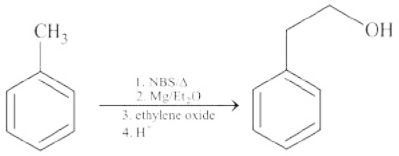


LEVEL - II

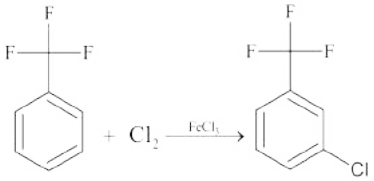
1. a)



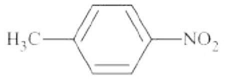
b)



c)

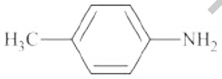


2. A =



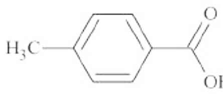
1-methyl-4-nitrobenzene

B =



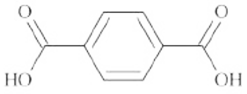
p-toluidine

C =



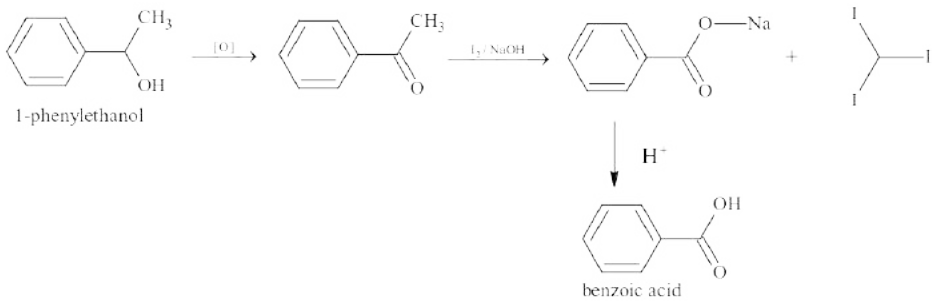
4-methylbenzoic acid

D =

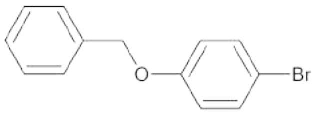


terephthalic acid

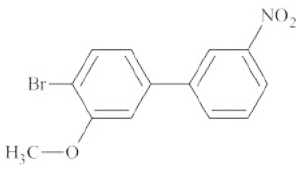
3. The reaction of $C_8H_{10}O$ with alkaline solution of iodine is an iodoform reaction. This reaction is possible if the compound D has $–CO_2 – CH_3$ or $– CH(OH) – CH_3$ group. The high carbon content in D indicates that D is an aromatic compound containing a benzene ring. To account for the given formula, the compound D may be $C_6H_5CH(OH)CH_3$. The given reactions are



4. a)

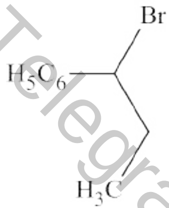


b)



5. a)

A =



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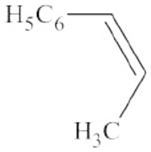

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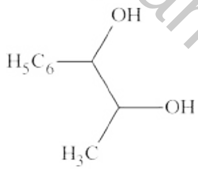

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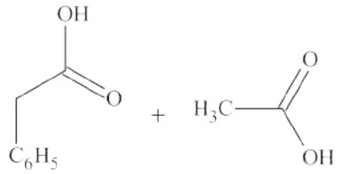
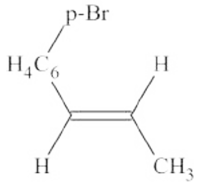


b)

E =



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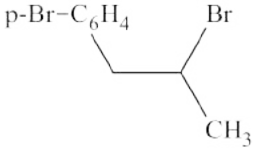
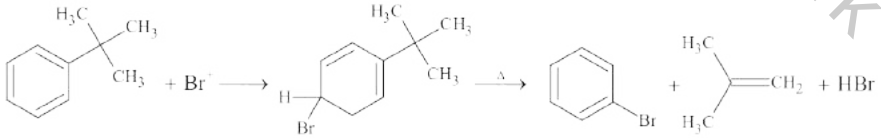
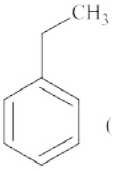
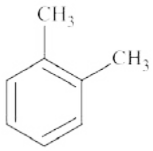
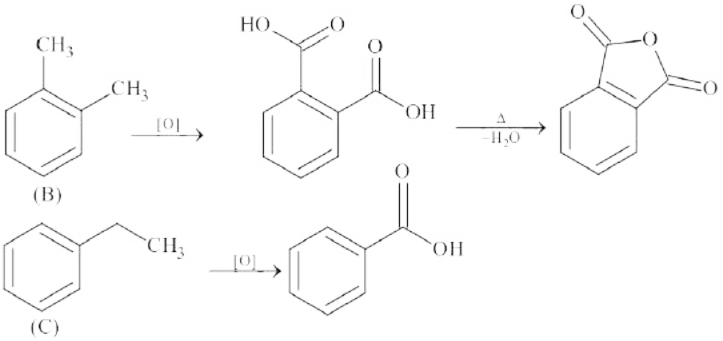


6. The Friedel-Crafts alkylation can be reversed especially when a 3° alkyl group such as Me_3C is present. Dealkylation is effected with Alr_3 by transfer of Me_3C^+ to another arene used as solvent, or at high temperature by protonation as H^+ and loss of Me_3C as $Me_2C = CH_2$.



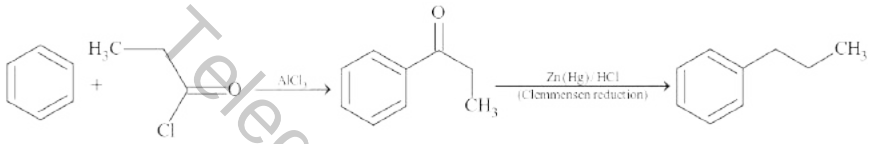
7. (A) is  (while (B) is 



(B)

(C)

8.



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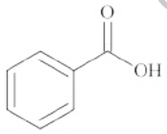
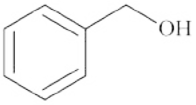
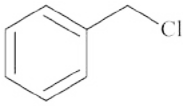
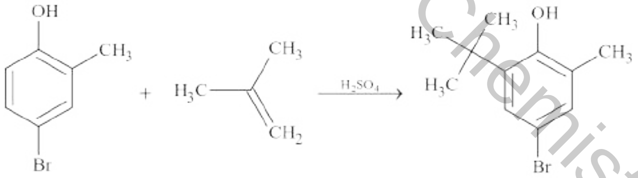
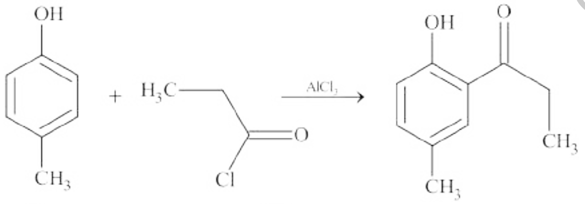
A = 
B = 
C = 

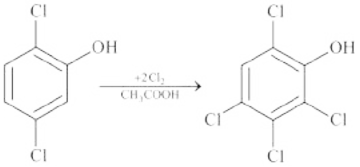
10. a)



b)



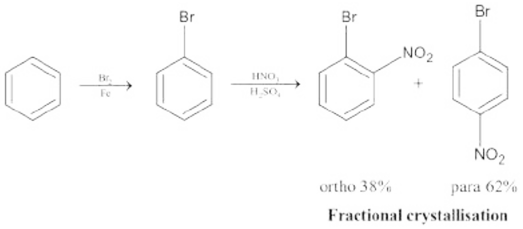
c)



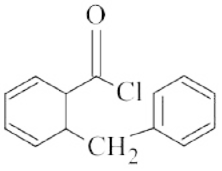
LEVEL - III

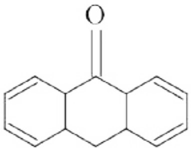
1. Phenyl group also can exert +R effect; in biphenyl one of the phenyl groups acts as electron donor and other electron acceptor. This makes biphenyl more reactive than benzene towards electrophilic substitution.

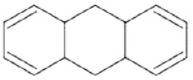
2.



3.

(A) 

(B) 

(C) 

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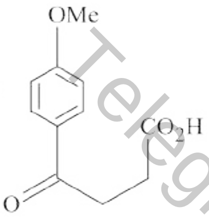
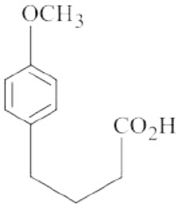
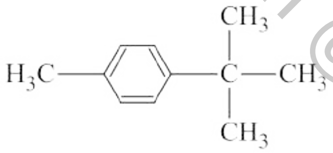
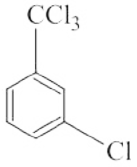
(A) 

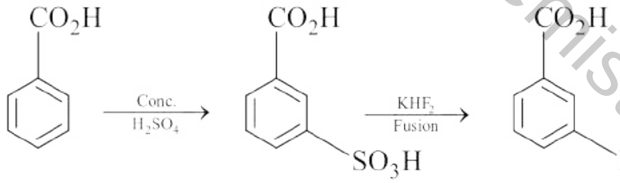
(B) 

5.

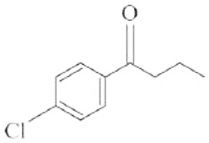
(i) 

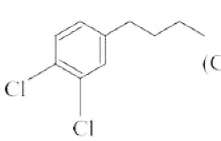
(ii) 

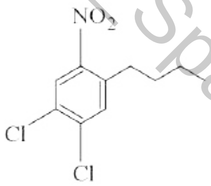
6.



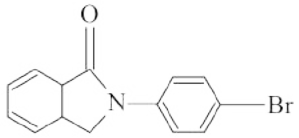
7.

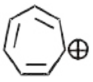
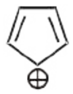
(A) 

(B) 

(C) 

8.



9.  is aromatic and hence exists as ion but the carbocation  will be antiaromatic and hence will not exists as ion even in presence of Ag^+ ion.